



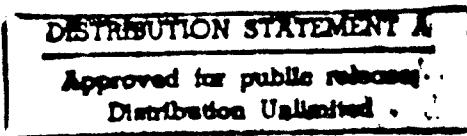
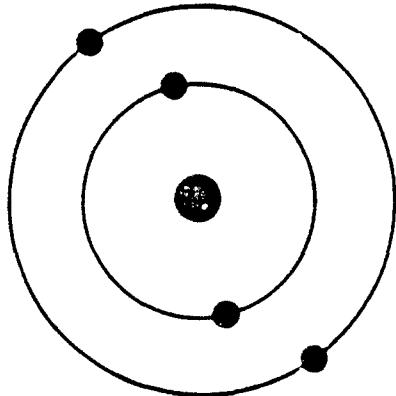
DTIC FILE COPY

# BERYLLIUM METAL SUPPLY OPTIONS

AD-A223 468

20030206079

DTIC  
ELECTED  
JUN 27 1990  
S E O B D



NATIONAL MATERIALS ADVISORY BOARD  
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS  
NATIONAL RESEARCH COUNCIL

90 06 26 100

**NATIONAL RESEARCH COUNCIL  
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS**

**NATIONAL MATERIALS ADVISORY BOARD**

The purpose of the National Materials Advisory Board  
is the advancement of materials science and engineering in the national interest.

**CHAIRMAN**

Dr. Bernard H. Kear  
Chairman, Dept. of Mechanics  
and Materials Science  
Dir., Center for Materials  
Synthesis  
College of Engineering  
Rutgers University  
P.O. Box 909  
Piscataway, NJ 08854

**PAST CHAIRMAN**

Dr. Arden L. Bement, Jr.  
Vice President, Technical  
Resources  
Science and Technology Dept.  
TRW, Inc.  
1900 Richmond Road  
Cleveland, OH 44124

**MEMBERS**

Dr. Norbert S. Baer  
Hagop Kevorkian Professor of  
Conservation  
New York University  
Conservation Center of the  
Institute of Fine Arts  
14 East 78th Street  
New York, NY 10021

Dr. Frank W. Crossman  
Assistant Director, Information  
Services  
Lockheed Missiles & Space  
Co., Inc.  
Org. 1466, Bldg. 102  
P.O. Box 3504  
Sunnyvale, CA 94088-3504

Mr. Edward J. Duhis  
President  
Crucible Research Center  
Crucible Materials Corporation  
P.O. Box 88  
Pittsburgh, PA 15230

Dr. James Economy  
Professor and Head of Materials  
Science  
University of Illinois  
1104 Green Street  
Urbana, IL 61801

Dr. Merton C. Flemings  
Professor and Chairman  
Department of Materials  
Science and Engineering  
Massachusetts Institute of  
Technology  
77 Massachusetts Avenue  
Cambridge, MA 02139

Dr. James A. Ford  
Vice President, Technology  
SEI/E Corporation  
P.O. Box 747  
Hendersonville, NC 28739

Dr. John K. Hulm  
Chief Scientist  
Westinghouse Research  
Laboratories  
1310 Beulah Road  
Pittsburgh, PA 15235

Dr. Melvin F. Kanninen  
Institute Scientist  
Southwest Research Institute  
P.O. Drawer 28510  
San Antonio, TX 78284

Dr. Robert A. Laudise  
Director, Physical and  
Inorganic Chemistry Research  
Laboratory, Room 1A-264  
AT&T Bell Laboratories  
Murray Hill, NJ 07974

Dr. David L. Morrison  
President  
IIT Research Institute  
10 West 35th Street  
Chicago, IL 60616

Dr. Donald R. Paul  
Melvin H. Gertz Regents Chair  
in Chemical Engineering  
Director, Center for  
Polymer Research  
University of Texas  
Austin, TX 78712

Dr. Joseph L. Penteost  
Professor  
School of Materials  
Engineering  
Georgia Institute of  
Technology  
Atlanta, GA 30332

Dr. John P. Riggs  
Vice President, R&D  
Research Division  
Managing Director, Mitchell  
Technical Center  
Hoechst Celanese Corp.  
86 Morris Avenue  
Summit, NJ 07901

Dr. Maxine L. Savitz  
Director  
Garrett Ceramic Components  
Division  
19800 South Van Ness Ave.  
Torrence, CA 90509

Dr. William P. Slichter  
AT&T Bell Laboratories  
(Retired)  
55 Van Doren Avenue  
Chatham, NJ 07928

Dr. Dale F. Stein  
President  
Michigan Technological  
University  
Houghton, MI 49931

Dr. John E. Tilton  
Coulter Professor  
Department of Mineral  
Economics  
Colorado School of Mines  
Golden, CO 80401

Mr. James R. Weir, Jr.  
Associate Director  
Metals & Ceramics Division  
Oak Ridge National Laboratory,  
P.O. Box X  
Oak Ridge, TN 37830

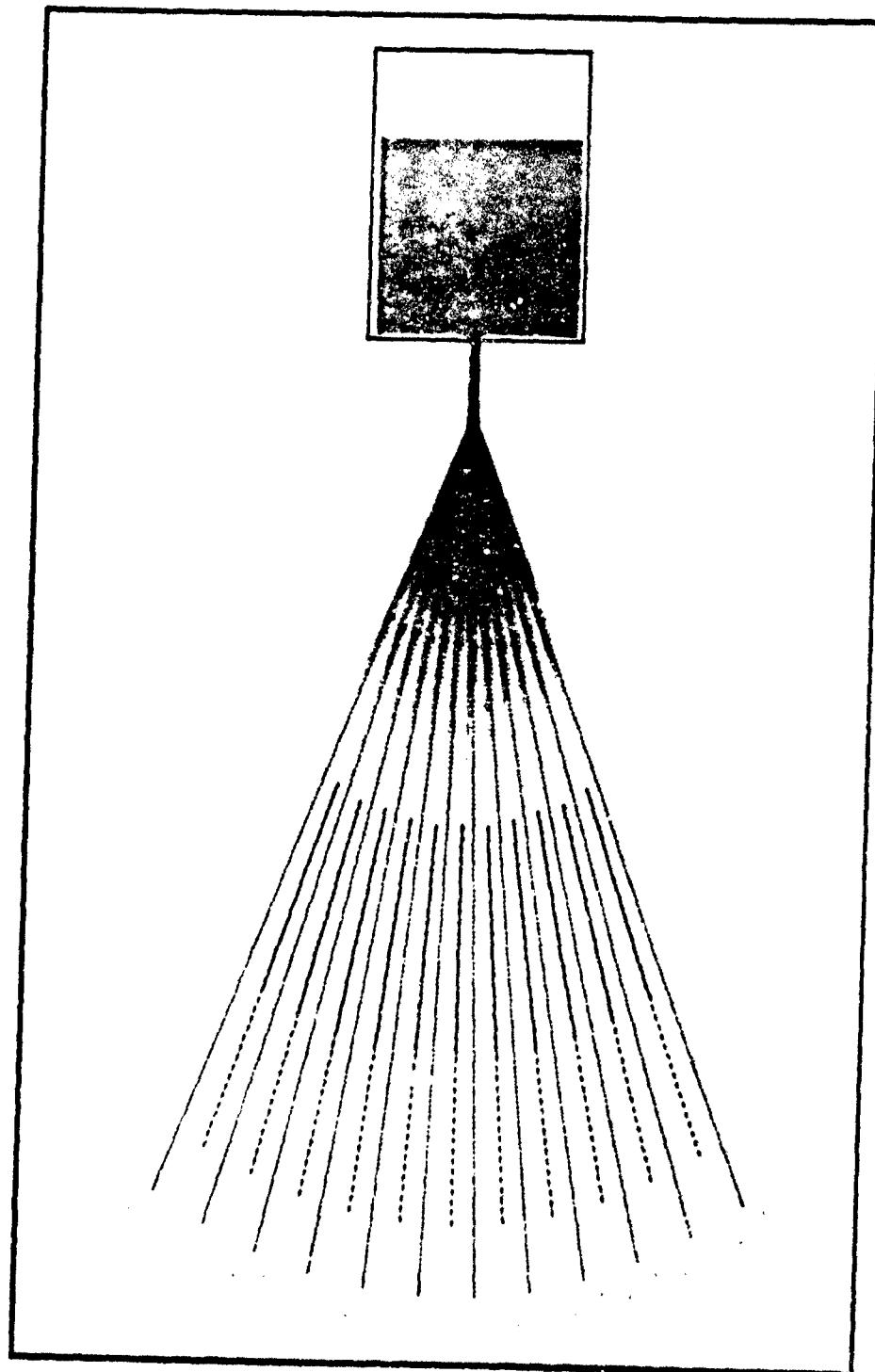
Dr. Robert M. White  
Vice President, Research &  
Engineering  
Control Data Corporation  
8100 4th Avenue South  
Minneapolis, MN 55440

Dr. James C. Williams  
General Manager  
Materials Technology Laboratories  
General Electric Company  
1 Neumann Way  
Cincinnati, OH 45215-6301

**NMAB STAFF**

K. M. Zwiskay, Director  
S. M. Barkin, Assoc. Director  
Mary Brittain, Adm. Officer  
2101 Constitution Ave., NW  
Washington, DC 20418

# **BERYLLIUM METAL SUPPLY OPTIONS**



# **Beryllium Metal Supply Options**

**Report of the Committee on  
Technologies for Preparing Beryllium Metal**

**NATIONAL MATERIALS ADVISORY BOARD  
Commission on Engineering and Technical Systems  
National Research Council**

**NMAB-452  
National Academy Press  
Washington, D.C.  
1989**

**NOTICE:** The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competencies and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

The National Academy of Sciences is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. Upon the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Frank Press is president of the National Academy of Sciences.

The National Academy of Engineering was established in 1964, under the charter of the National Academy of Sciences, as a parallel organization of outstanding engineers. It is autonomous in its administration and in the selection of its members, sharing with the National Academy of Sciences the responsibility for advising the federal government. The National Academy of Engineering also sponsors engineering programs aimed at meeting national needs, encourages education and research, and recognizes the superior achievements of engineers. Dr. Robert M. White is president of the National Academy of Engineering.

The Institute of Medicine was established in 1970 by the National Academy of Sciences to secure the services of eminent members of appropriate professions in the examination of policy matters pertaining to the health of the public. The Institute acts under the responsibility given to the National Academy of Sciences by its congressional charter to be an advisor to the federal government and, upon its own initiative, to identify issues of medical care, research, and education. Dr. Samuel O. Thier is president of the Institute of Medicine.

The National Research Council was organized by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and advising the federal government. Functioning in accordance with general policies determined by the Academy, the Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in providing services to the government, the public, and the scientific and engineering communities. The Council is administered jointly by both Academies and the Institute of Medicine. Dr. Frank Press and Dr. Robert M. White are chairman and vice chairman, respectively, of the National Research Council.

This study by the National Materials Advisory Board was conducted under Contract No. MDA903-87-C-0635 with the U.S. Department of Defense and U.S. Department of Energy.

This report is available from the Defense Technical Information Center, Cameron Station, Alexandria, VA 22304-6145.

Printed in the United States of America

## DEDICATION

The NMAB Committee on Technologies for Preparing Beryllium Metal dedicates its report to a man whose professional ability and devotion to government security efforts made him an invaluable asset to the Department of Energy. Dr. Richard J. Jiaoletti, Program Engineer at the Albuquerque Operations Office of the Department of Energy, acted as coordinator for various beryllium-related and other critical government development activities and was instrumental in initiating the request for an independent assessment by the National Research Council of the current domestic beryllium metal supply capability. He was uniquely qualified to act as principal liaison for the NRC study program, handling the rather sensitive production issues in an even-handed, unbiased manner. His ability to explain complex technical problems in a straightforward way permitted a logical analysis of each problem area that led to meaningful discussions of alternative solutions. These attributes are recognized by his co-workers and peers, and we will miss his guidance and advice. The committee and the NMAB staff regret that he is not here to share in the product of this effort.



Accession For	
NTIS GRA&I <input checked="" type="checkbox"/>	
DTIC TAB <input type="checkbox"/>	
Unannounced <input type="checkbox"/>	
Justification _____	
By _____	
Distribution/ _____	
Availability Codes	
Distr	Avail and/or Special
A-1	

## ABSTRACT

The importance of an uninterrupted supply of beryllium metal for the U.S. military and aerospace effort is described. The means by which the single supplier in the western world could meet present and future environmental requirements is examined. In view of the small quantity of metal needed, the size of the total market, and the present status of alternate processes, it would be most advantageous to upgrade existing extractive metallurgical facilities. The most environmentally sound and cost-effective fabrication techniques were found to be the enclosed powder gas atomization process and the near-net-shape processing of products. To ensure the metal supply, with the necessary fraction of needed high-purity material, government control of scrap for recycling and electrorefining is required. An acceptable level of worker exposure to beryllium cannot be quantified at this time, and therefore it is necessary to operate equipment so as to ensure that airborne beryllium is reduced to the minimum feasible level. It is suggested that all U.S. government agencies with beryllium activities coordinate their efforts with the interagency Beryllium Coordinating Committee and continue close liaison with related activities at the Royal Ordnance Factory, Cardiff (U.K.).

*On the cover: The Bohr atomic model of beryllium*

*Frontispiece: Metal atomization (courtesy of Crucible Research)*

## PREFACE

Beryllium is not a common metal and is not well known in metallurgical and other technical areas. It does possess some special characteristics that are vital to a number of critical and strategic government programs, because of its low weight, high strength, stiffness, and corrosion resistance.

This study was requested to obtain an independent assessment of options prepared for the Department of Defense and the Department of Energy by the interagency Beryllium Coordinating Committee. These options are actions recommended for ensuring the uninterrupted supply of beryllium metal in the quality and quantities required to meet current and future government needs. Because the current situation of one domestic (and western world) supplier presented a serious concern to the Department of Energy and the Department of Defense, an examination of alternative technologies that may alleviate this problem was requested. This assessment is primarily a technical one, but metal production is so closely tied to environmental and medical factors that the committee has included these issues in its report.

The small industrial base for the production of this metal made the selection of the committee difficult. People were sought who have no present, or only a minor, connection with processors of the metal. In this way, no serious bias would be involved in the decisions rendered by the study program. Many of the committee members had prior experience in beryllium extraction and process metallurgy. Some, however, have backgrounds not related to beryllium but extensive experience in plant design, unit processes, materials flow, and engineering that can be related directly to a chemical and metals production facility. This mix of disciplines was deemed necessary to obtain a broad-based and open-minded assessment of the technical factors affecting the production of beryllium metal.

The inputs received and the responses to specific questions set forth by the committee provided the basis for prioritizing the Beryllium Coordinating Committee's options and for developing additional options for action that are appropriate for maintaining uninterrupted production. The committee made extensive use of the information it gathered in committee meetings and has presented the government a technically based set of recommendations for actions that could ensure the ready availability of this unique metal while still protecting the health and safety of workers.

## ACKNOWLEDGMENTS

The committee is grateful to a number of individuals who provided extensive background materials for committee use. Richard R. Corle of the Rocky Flats plant (under Rockwell International management contract with DOE to manufacture special components from metal purchased from Brush Wellman, Inc.) furnished copies of reports prepared for the Beryllium Coordinating Committee (BCC) on beryllium processing and arranged for the following oral presentations on February 18, 1988, by members of the Rocky Flats plant technical staff: S. P. Abeln on beryllium powder technology development and on beryllium near-net-shape technology; D. L. Mitchell on beryllium electrorefining; and F. J. Furman on chronic beryllium disease investigations at Rocky Flats. Hugh D. Hanes of Brush Wellman Inc. (BWI) furnished copies of reports prepared for the BCC on beryllium processing and arranged for the following oral presentations on February 18, 1988, by members of the Elmore, Ohio, beryllium production facility staff: A. W. Astle on Tasks I and II (R&D Study for Optimization of Beryllium Production Operations); D. J. Kaczynski on beryllium reduction technologies and review of Task V (Final Report); and J. Marder on inert gas atomization.

The committee was privileged to be permitted to have a first-hand examination of BWI's beryllium production facility at Elmore on April 5 and 6, 1988. Arrangements were made by Hugh D. Hanes, assisted by his secretaries, Helen Petersen and Julie Booth. Mr. Hanes was the host and coordinator for the technical briefing and plant tour. The discussion leaders of sessions were A. W. Astle on facility capital expenditures, K. Brown on waste management, D. J. Kaczynski on a conceptual beryllium extraction facility, M. Kuxhaus on the near-net-shape program, J. Marder on powder atomization, M. Powers and T. Markham on medical programs, and P. Wilson on plant health and safety programs. Mr. Hanes presented a final summary and some pertinent financial data for committee use. The Elmore plant tour included the entire facility, and the staff gave unrestricted answers to all questions. In addition, BWI president and CEO, Ray Foos, is thanked for meeting with the committee to present a perspective of the future plans for the Elmore facility.

Inputs from staffs of the Rocky Flats plant and BWI's Elmore plant were crucial to the committee's understanding of the factors that affect the production of beryllium metal and what efforts are being made to continuously update this capability. These generous contributions and efforts on the

committee's behalf are acknowledged with thanks. A special mini-meeting was held at the Rocky Flats plant in Golden, Colorado, on April 15, 1988. The two medical members of the committee, Roy Albert and William Nicholson, conferred with the medical staff at this facility on their activities and data-collection efforts on beryllium exposure effects in the workplace and the neighborhood. These discussions were invaluable in preparing the chapter on Workplace Health Considerations and Monitoring, and the participants, particularly Kathlene Kreiss of the National Jewish Center for Immunology and Respiratory Medicine, Lee S. Newman of the Department of Preventive Medicine and Biometrics, University of Colorado School of Medicine, and F. J. Furman of the Rocky Flats plant medical department, are thanked for their cooperation. In addition, Dr. Kreiss graciously reviewed the health section of Chapter 7 and offered constructive suggestions on its content.

The committee also acknowledges with thanks the discussions of a proposed second supplier of beryllium metal on May 12, 1988. Presentations were made by Robert A. Charpie of the Cabot Corporation on the Cabot/Cyprus joint venture into beryllium metal production, Walter F. Greeley of the Cabot Corporation on Cabot's diverse product line and the basis for its re-entry into the beryllium metal market, Tony J. Hickl of the Advanced Metallurgical and Testing Corporation (formed by Cabot Corporation and Cyprus Minerals Company) on a proposed venture into a new beryllium production capability, and Bruce Wright of Cyprus Minerals Company on mining and beneficiation of beryllium ores. Peter M. Jarowey of the Cabot Corporation is thanked for arranging these presentations.

Powder metallurgy for preparing complex shapes of beryllium offers numerous advantages and opportunities. The technology of gas atomization was examined in some detail by the committee, and assistance was given by oral presentations from experts currently working in this field on July 13, 1988. The following are thanked for their participation in a gas atomization discussion before the committee: Iver E. Anderson of Ames Laboratory, who discussed ultrasonics for metal atomization; Frank S. Biancaniello and Steve S. Ridder of the National Institute of Standards and Technology, who discussed in situ particle size measurement in gas atomization; Wayne Castledine of Special Metals Corporation, who discussed commercial gas atomization; and C. Fred Yolton of Crucible Research, who discussed gas atomization and near-net-shape processing. In addition, B. Pinto and J. Marder of the Brush Wellman staff described their activity in beryllium metal atomization and identified where efforts will be directed in the future.

The government liaison representatives are thanked for participating in committee discussions and providing valuable support materials and data for committee use. They were most helpful in assisting the committee in defining the scope of the study and offering needed guidance during the development of the committee's report drafts. Richard J. Jiaocletti of DOE, Albuquerque,

Cynthia E. Gonsalves of DOD, and Richard R. Corle as the BCC representative are given special acknowledgment for the extra effort they made to provide the committee with detailed data on processing, both old and new. The two technical advisors, Loren A. Jacobson of the Los Alamos National Laboratories and Gilbert J. London of the Naval Air Development Center, have had wide experience in beryllium and were an asset to the committee in identifying specific problem areas. Fred Fulton, former BCC member, is thanked for his review of earlier BCC activities. In addition, the committee appreciates the prompt response to its request for background data on the beryllium industry occupational health standard from Bea Proctor of the Technical Information Branch and William Halperin of the Industrywide Studies Branch, NIOSH Center for Disease Control, Robert A. Taft Laboratories in Cincinnati. Morton Wong of UNOCAL is thanked for providing the committee published data on earlier work and patents on the Bureau of Mines efforts on electrowinning of beryllium.

The chairman of the committee thanks the members for their dedication and for the patience shown during the numerous iterations and revisions of the report drafts. Particular thanks go to committee members who served as chapter or section coordinators to assemble pertinent facts for various parts of the report and for presenting the data in a timely open-minded and professional manner.

On behalf of the committee, the chairman thanks George Economos, NMAB Program Officer, and Aida Neel, Senior Secretary at NMAB, for their untiring assistance to the committee during its deliberations and report writing.

*W. D. Manly  
Chairman*

## **COMMITTEE ON TECHNOLOGIES FOR PREPARING BERYLLIUM METAL**

### *Chairman*

WILLIAM D. MANLY, Consultant, Kingston, Tennessee

### *Members*

ROY E. ALBERT, University of Cincinnati, Cincinnati, Ohio

JAMES E. COYNE, Wyman Gordon Company, Worcester, Massachusetts

EDWARD J. DULIS, Crucible Research, Pittsburgh, Pennsylvania

STANLEY H. GELLES, Gelles Laboratories, Inc., Columbus, Ohio

KENNETH B. HIGBIE, Consultant, Stroudsburg, Pennsylvania

NOEL JARRETT, Noel Jarrett Associates, Lower Burrell, Pennsylvania

WILLIAM J. NICHOLSON, Mt. Sinai Medical Center, New York, New York

MARTIN B. SHERWIN, W.R. Grace & Co., Columbia, Maryland

MORGAN C. SZE, Consulting Engineer, Portsmouth, New Hampshire

### *Technical Advisors*

LOREN A. JACOBSON, Los Alamos National Laboratories, Los Alamos, New Mexico

GILBERT J. LONDON, Naval Air Development Center, Warminster, Pennsylvania

### *Liaison Representatives*

RICHARD E. CORDER, Office of the Assistant Secretary of Defense, Strategic and Critical Materials Directorate, Washington, D.C.

RICHARD R. CORLE, Rocky Flats Plant (Rockwell International Corporation), Golden, Colorado

**CYNTHIA E. GONSALVES, Department of Defense, Washington, D.C.**

**RICHARD J. JIACOLETTI, U.S. Department of Energy, Albuquerque, New Mexico**

**RAYMOND J. DUNDON, Department of Defense, Defense Logistics Agency, Washington, D.C.**

*NMAB Staff*

**GEORGE ECONOMOS, Senior Program Officer**

**AIDA NEEL, Senior Secretary**

## **CONTENTS**

### **EXECUTIVE SUMMARY 1**

#### **Chapter 1 CONCLUSIONS AND RECOMMENDATIONS 7**

Major Conclusions 7  
Major Recommendations 8  
Priority Listing 9

#### **Chapter 2 INTRODUCTION 11**

#### **Chapter 3 CURRENT BERYLLIUM PRODUCTION FACILITIES 13**

Existing Process 13  
Recent Changes in Beryllium Production Processes 18  
Conclusions and Recommendations 23  
References 24

#### **Chapter 4 ALTERNATE METALLURGICAL EXTRACTION TECHNIQUES 25**

Advanced Magnesium Reduction 25  
Sodium Reduction 27  
Electrowinning 32  
Electrorefining 37  
Cost Considerations 42  
Conclusions and Recommendations 46  
References 47

#### **Chapter 5 IMPROVED METALLURGICAL OPERATIONS 51**

Inert Gas Atomization 51  
Near-Net-Shape Processing 52  
Environmental and Cost Considerations 53  
Summary 54  
Conclusions and Recommendations 57  
References 58

#### **Chapter 6 SCRAP RECYCLING 59**

Current Status 59  
Trends 62  
Conclusions and Recommendations 65  
References 66

#### **Chapter 7 WORKPLACE HEALTH CONSIDERATIONS AND MONITORING 67**

Health Considerations 67  
Beryllium Monitoring Results 70

**Chapter 7 (*Continued*)**

Beryllium Sampling Strategies	76
Applicable Regulations	80
Conclusions and Recommendations	81
References	83

**Appendix A EXCERPTS FROM NATIONAL STOCKPILE PURCHASE  
SPECIFICATIONS 87**

**Appendix B BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS 101**

## **EXECUTIVE SUMMARY**

The unique properties of beryllium metal are critical to a number of U.S. defense and aerospace programs, such as reflectors or moderators in nuclear reactors, gyroscopes, computer parts, and inertial guidance instruments, and therefore it is essential that a continuous uninterrupted supply of the metal be available. Only one western world supplier exists today, Brush Wellman Inc. (BWI), which supplies the required quantity and quality of the metal primarily for government use. A critical situation results when there is a disruption in the supply train. In addition, health and environmental pollution effects are a major issue that affects the production of the metal and fabricating final shapes. Exposure of factory personnel must be kept to a minimum. The producer must take extensive precautions to meet or stay below the permissible OSHA particulate exposure limit of 2 micrograms per cubic meter each 8-hour workday at every work station.

Accidents and equipment failures have occurred and continue to occur, but at less frequent intervals today, as compared with past experiences. Beryllium particulate limits are exceeded that lead to periodic area or plant evacuations. Such episodes cause a disruption in plant output and raise serious concerns in the agencies involved. The Department of Defense and Department of Energy, the principal customers for the metal, have concerns with the causes and effects of these interruptions and have, since 1981, supported a joint Beryllium Supply Program to ascertain what government actions would be appropriate to ensure the supply of the metal. The Beryllium Coordinating Committee (BCC) was established later to furnish technical advice and guidance in this area. Four production plant options were developed by the BCC as possible actions for the future production of the metal:

1. Construction of a new beryllium metal production facility,
2. Construction of a scrap recycling facility,
3. Combination of 1 and 2 in a single facility; and
4. Upgrading the existing production facility to incorporate new production technologies and processes and their control.

The National Materials Advisory Board committee was asked by DOD and DOE to assess the BCC options and, where appropriate, to present other options developed in its findings.

This NMAB study critically examines the current BWI production facility, assesses alternate metallurgical extraction techniques, identifies improved metallurgical operations, evaluates various scrap recycling methodologies, and examines the health considerations and monitoring techniques applicable to the workplace. Discussions with experts in these areas and direct examination of BWI's beryllium production facility in Elmore, Ohio, provided the committee with the necessary technical data base to develop specific recommendations for action.

The current process at the Elmore facility evolved from the processes used in the 1940s but with changes to correct specific problems. Processing starts with beryllium hydroxide concentrate entering the plant. This is converted to ammonium beryllium fluoride (ABF) by treatment with ammonium hydrogen fluoride. The purified product is dried and calcined to produce beryllium fluoride. Magnesium metal is reacted with beryllium fluoride to produce beryllium metal pebbles, magnesium fluoride, and beryllium fluoride (in excess of the magnesium metal used). The beryllium metal pebbles are separated (the excess beryllium fluoride is recycled) by a sink-float operation and carefully processed to produce a 98 percent pure product. The metal, with scrap added, is vacuum-cast into ingots that serve as the feedstock for the powder-making operation.

The as-cast billets are not used as such but are machined on a lathe to produce chips that are further reduced in size by attritioning, impact grinding, or ball milling to produce a metal powder. Chemical and particle size analysis and x-ray inspection are used to ensure the purity and quality of the powder. Various lots, based on their chemistry and powder size characteristics, are blended and packed into appropriate dies for consolidation by vacuum hot pressing (VHP), hot isostatic pressing (HIP), cold isostatic pressing (CIP), or near-net-shape (NNS) fabrication.

Efforts to optimize various beryllium production operations have been initiated in recent years, especially those that have had episodes of being "out of control" as regards high airborne beryllium particle concentrations. Wet-process operations give the least control problems. Dry operations, such as the ABF drying and decomposition operations, chip grinding, and final machining and polishing operations, require constant operator attention and proper equipment maintenance procedures to minimize personnel exposure to particulates. Work on design changes for the ABF decomposition furnace exemplifies the type of process improvement possible in existing unit processes.

Alternative extractive techniques offer opportunities for improvement in process yield and environmental control. Some changes currently under consideration include beryllium fluoride reduction under an inert atmosphere, the addition of a third salt to lower the melt viscosity in the reduction furnace, the possible use of a tall reactor for continuous or

semicontinuous operation, and the use of improved instrumentation and equipment leading to a totally enclosed or remote operation.

Sodium reduction of beryllium chloride, as is used in titanium and zirconium metal production (Kroll process), is a possible alternative; sodium reduction of beryllium fluoride has inherent separation problems. A side-by-side comparison of the current magnesium-reduction fluoride process with the sodium-reduction chloride process and the related costs shows some advantages for the sodium process. Actual process tests have yet to be performed, and at this time oversimplification of the available process and cost data casts doubts on the validity of the assumptions employed in the comparison. Kroll technology data from commercial titanium or zirconium production activities could be useful in this comparison. The R&D time and high development costs involved make it difficult to justify pursuing this alternate technology in view of the limited market for the product.

The direct electrolytic reduction of metallic beryllium, as in aluminum production, could offer numerous advantages in process control and environmental hazard reduction. The higher melting point of beryllium, 1287°C, compared to aluminum, 660°C, and the present lack of an electrolyte that will dissolve beryllium oxide are major problems needing resolution. Extensive earlier work by the U.S. Bureau of Mines provides much background data on electrowinning of beryllium and identifies where R&D should be directed to move the process toward commercialization. A number of other electrowinning processes have been explored, each of which requires extensive development work for its advancement. In each, the economics of the process offers little incentive to invest the time and funds necessary to develop the technology directly to beryllium. On the other hand, electro-refining is used to produce high-purity beryllium metal from a lesser grade of metal. The process removes most of the metallic impurities and yields plate-like crystals that can be easily consolidated into a more processible metal form. Only limited quantities of this high-purity metal are needed, so, at best, a small-scale facility could easily supply the material needed for special-application end-product forms of the metal. Estimated cost projections, comparing 1982 with 1992 data and incorporating improved or new processing technologies, indicate that only marginal cost improvement can be anticipated (approximately 6 percent overall).

An assessment was made of improved metallurgical operations that could provide better environmental control and produce a final metal shape having high density and suitable microstructure properties. The gas atomization metal powder route offers numerous advantages. The basic technology is well established and is employed commercially in superalloy, titanium, and other specialty metals powder production. A spherical free-flowing powder having high packing density is produced, characteristics not achieved by the existing chip-to-powder preparation method. Near-net-shape fabrication

4

technology is applicable to yield HIP density of 100 percent. The material savings alone can be as high as 90 percent compared to the existing billet-machining, chip-grinding powder route. Small-scale tests at BWI have confirmed this potential, and a scale-up of the process will provide the basis for a commercial-scale facility. A second scrap recycling and NNS production facility employing this technology is recommended to ensure the continuing supply of the consolidated metal and a NNS fabrication capability. It is understood that the two technologies would exist together because each has its own impact on the final product.

Scrap recycling is an important source of the metal that reduces the strain on the initial metal-producing facility. Today, in-house scrap at BWI is routinely recycled, whereas DOD subcontractor scrap is sold on the open market and DOE inventories its in-house scrap (Rocky Flats plant operations). This DOD and DOE scrap could act as a source of supply for the powder-producing facility, in both the existing machining-to-chip grinding process and the gas atomization process now under development. Electrorefining is the technology for upgrading the recycled scrap. Cost estimates and comparisons indicate considerable savings in materials and processing costs. A substantial reduction in scrap production results from employing the NNS technology.

It is understood that existing health considerations and monitoring of the workplace for personnel exposure to beryllium particulates are essential to ensure continuous operation of the beryllium-producing facility. This report reviews the historical development of the OSHA standard of 2 micrograms per cubic meter per 8-hour workday. Meeting this upper limit in the workplace consistently has been difficult, and incidents have required workplace or plant evacuations until the problem has been corrected. Chronic berylliosis and lung cancer among employees are the concern of the medical staffs of these facilities. Sufficient and accurate background exposure data are lacking. These would provide a sound scientific data base for establishing recommended exposure limits. The report reviews plant data indicating that worker sensitivity and susceptibility varies and no criterion can be set on what is a minimum acceptable threshold of beryllium exposure. It is generally agreed that occupational exposure should be reduced to the greatest extent feasible. In addition, it is noted that the beryllium-related lung cancer rate is low compared to the risk associated with the standards for other carcinogens.

Monitoring techniques for beryllium particulates in the workplace include high-volume air samplers, worker lapel samplers, respirator data, and swipe samples. Daily weighted averages and time-weighted averages are used to monitor and record beryllium workplace particulates. Deficiencies in the monitoring techniques and programs are identified and generally involve improper use of respirators, lack of detailed monitoring during upset conditions, averaging of an area and not an individual's exposure

during the performance of critical operations, and compulsory periodic medical checks on individual workers. Improvements in reducing worker exposure have been implemented, and high-risk areas received particular attention. Independent studies of work areas have identified places where monitoring variability can occur and assessed the usefulness of different sampling methods. Additional sampling methodology research is recommended. Generally, maintaining a clean factory facility and adhering to well-founded process-control procedures go far in reducing environmental upset situations, with subsequent worker exposure hazard. Activities at the Royal Ordnance Factory in Cardiff (U.K.) in recycling, housekeeping, and monitoring of the workplace could provide additional guidance in initiating appropriate corrective measures. Recommendations include actions on an expanded and improved monitoring program, an increase in housekeeping personnel involved and their added activities, a continuing review of processing technology toward employing state-of-the-art engineering, and investigations into real-time monitoring devices.

Finally, the committee recommends as a first priority upgrading of the existing facility, which includes adding gas atomization powder production and expanding NNS fabrication capability. In addition, a separate new scrap recycling facility should be established to ensure an added production capability of this critical metal to meet government quality and quantity requirements.

## **Chapter 1**

# **CONCLUSIONS AND RECOMMENDATIONS**

The committee has made a critical examination of the current manufacturing processes for preparing beryllium metal and has identified various areas where improvements can best be made. The principal conclusions and recommendations for action, based on discussions in subsequent chapters of this report, are listed here. Each chapter contains more specific conclusions and recommendations that are closely related to the data presented there.

## **MAJOR CONCLUSIONS**

1. Currently there is no alternative extraction process for beryllium metal production ready for commercialization, other than the magnesium-reduction process, and the identified market offers little incentive to develop one.
2. Much environmental improvement is believed possible within the current magnesium-reduction extraction process.
3. The process of gas atomization and near-net-shape fabrication should substantially reduce environmental contamination and processing costs. Near-net-shape processing will significantly reduce both process and machining scrap, which will affect positively both environmental and cost factors.
4. The basic technology for gas atomization is already in place, based on established commercial powder metallurgy superalloy production.
5. The amount of scrap generated by DOD is significantly greater than that generated by DOE and is not controlled.
6. There is a small need for high-purity beryllium for special applications derived from a stand-alone scrap-reclamation facility.
7. Electrorefining of beryllium metal scrap has had sufficient development to be ready for commercial implementation.
8. To ensure effective technology development and applications, it is

important to maintain a government-controlled source of expertise in beryllium processing and metallurgy.

9. A need exists for improved coordination among and within government agencies involved in beryllium activities.

10. Present beryllium exposure monitoring is inadequate in the primary facility.

11. It is possible that chronic berylliosis and beryllium-induced lung cancer represent processes where no fixed threshold concentration can be regarded as being completely safe for everyone.

#### MAJOR RECOMMENDATIONS

1. Focus efforts toward upgrading existing facilities and processes rather than pursuing completely new technologies for the extraction of beryllium; direct special efforts to the decomposition of ammonium beryllium fluoride (ABF) and the magnesium reduction of beryllium fluoride.

2. Displace the current beryllium powder-production method by gas atomization.

3. Advance and utilize near-net-shape technology in the making of beryllium hardware.

4. Conduct expanded R&D programs that are needed in support of recommendations 1, 2, and 3, separate from the primary facility efforts.

5. Establish a separate facility for electrorefining, scrap recycling, gas atomization, and near-net-shape consolidation, thereby ensuring an added material and shape fabrication capability.

6. Initiate methods for the control of DOD scrap similar to those used by DOE.

7. Develop a mechanism to expand the role of the interagency Beryllium Coordinating Committee to help handle the overall coordination of beryllium activities for the government.

8. Expand and improve the beryllium monitoring system to include personal monitors and swipe samples as is done in the facility at the Royal Ordnance Factory, Cardiff (U.K.).

9. Continue efforts to reduce worker exposure to the minimum feasible level by employing engineering control methods that are uniquely qualified

to produce the required plant environment so as to maintain *in all cases* exposure levels below the OSHA-mandated levels.

### PRIORITY LISTING

In addition to presenting these selected recommendations, the committee reviewed the options for actions that had been developed by the Beryllium Coordinating Committee (see Chapter 2 for details). Table 1-1 lists the options in the order received by the committee, and a priority number is placed beside each. The basis for the priority rating is in terms of the technical and economic factors considered, and comments are offered where applicable. The table is a bird's-eye view of the overall actions to be considered by the sponsors. Obviously, actions on the more detailed recommendations developed by the committee offer the best opportunity for ensuring an uninterrupted production of beryllium metal.

**TABLE 1-1 Decision Packet: Beryllium Coordinating Committee Options**

Priority*	Option	Factors Considered					
		Technical		Economic		Comments	
		Favorable	Unfavorable	Favorable	Unfavorable		
3	Construction of new facility						
3	a. New process	X		X		High capital cost and timing too long	
6	b. Magnesium reduction	X		X		High capital cost and timing too long	
2	New scrap recycling facility	X		X		As a separate facility	
	Combination of the two above in one facility					Separate actions advised	
1	Upgrading existing facility	X		X		Includes powder by gas atomization and near net-shape forming	

\* Filing sequence is as developed by the BCC; priority number is the committee's recommendation for action.

## Chapter 2

# INTRODUCTION

Beryllium, element number 4 in the periodic table of elements, is a unique lightweight, strong, stiff, corrosion-resistant, and strategically important metal. The metal is essential for some government production programs; at present there are very few acceptable replacement materials, and even these are for very specific, low-volume applications. Today, there is only one producer of the metal in the western world, Brush Wellman Inc. (BWI) in Elmore, Ohio.

The ability to meet environmental regulatory standards for airborne beryllium and its compounds is difficult, and this sometimes restricts metal production. Since the federal government is the principal customer for beryllium metal and the total government requirement (which has fluctuated over the years) represents a limited fraction of the entire beryllium market (metal, alloys, and oxide), there is concern about having a ready supply of the metal for government purposes. Anticipated government requirements for the metal are a total of about 60,000 lb deliverable over the next 2 years (1989-1990) to the National Defense Stockpile<sup>1</sup> and an estimated 100,000 lb per year for the next 5 years (1988-1992) for DOD and DOE needs. A joint DOD and DOE Beryllium Supply Program (BSP) was initiated in 1981 to determine what actions are needed to provide for an assured metal supply, both in terms of quality and quantity. The Beryllium Coordinating Committee (BCC) was established later to serve as the principal source of technical advice for the BSP and to provide technical guidance to DOE in Albuquerque, New Mexico. The BCC developed four production plant options as possible courses of action for the future production of beryllium metal:

1. Construction of a new beryllium metal production facility;
2. Construction of a scrap recycling facility;
3. Combination of options 1 and 2 in one facility;

---

<sup>1</sup>GSA purchased (June 28, 1988) for the National Defense Stockpile about 60,000 lb of three grades of beryllium metal (see Appendix) from Brush Wellman Inc. for an approximate value of \$19,000,000, deliverable over a 2-year period (the weight and price are approximate because of the nonstandard billet size).

4. Upgrading the existing production facility to incorporate new production technologies and processes and their control.

These actions could be either private or government-financed, or possibly a joint endeavor; both the ownership and the management of the facility are involved. In addition, the sponsors asked the committee to present other options developed in its findings.

The NMAB Committee on Technologies for Preparing Beryllium Metal was convened to examine the BCC options and to develop additional options based on technical and economic factors as may be appropriate. The expertise represented on the committee included chemical engineering, metallurgical engineering, plant design and industrial economics, metals extraction and processing, and environmental and health concerns. The assessment begins with the assumption that the availability of the starting material, beryllium hydroxide, is adequate and proceeds from this point to the processing through to the finished part. The charge to the committee was to prioritize the options based on such issues as available cost estimates, ability to meet current and future potentially more restrictive OSHA regulations, impact of probable plant locations, and advice regarding plant ownership and management.

The committee held five meetings in Washington, D.C., and toured BWI's beryllium production facility in Elmore, Ohio. The staffs of the BWI plant, the Rocky Flats plant (under Rockwell International management contract with DOE), and the Lawrence Livermore Laboratory provided oral presentations and written documentation for committee use. The BWI plant tour gave the committee members a first-hand view of how the metal is produced and then fabricated into final shapes and what precautions are taken to ensure the safety of workers and the neighboring environment. In addition, information was made available from BSP-sponsored studies on production operations, optimum fabrication technologies, and scrap recycling, including detailed technical and economic data related to these processes. Information was also received on a possible second supplier entering the field and on gas atomization of metal powder as an effective alternate processing technology.

These inputs provided an extensive background data base with which the committee could work. A major objective of the committee report is to provide the government with a "decision package" for the selection of an action option to ensure a future capability for producing beryllium metal to meet anticipated DOD and DOE needs.

## Chapter 3

### CURRENT BERYLLIUM PRODUCTION FACILITIES

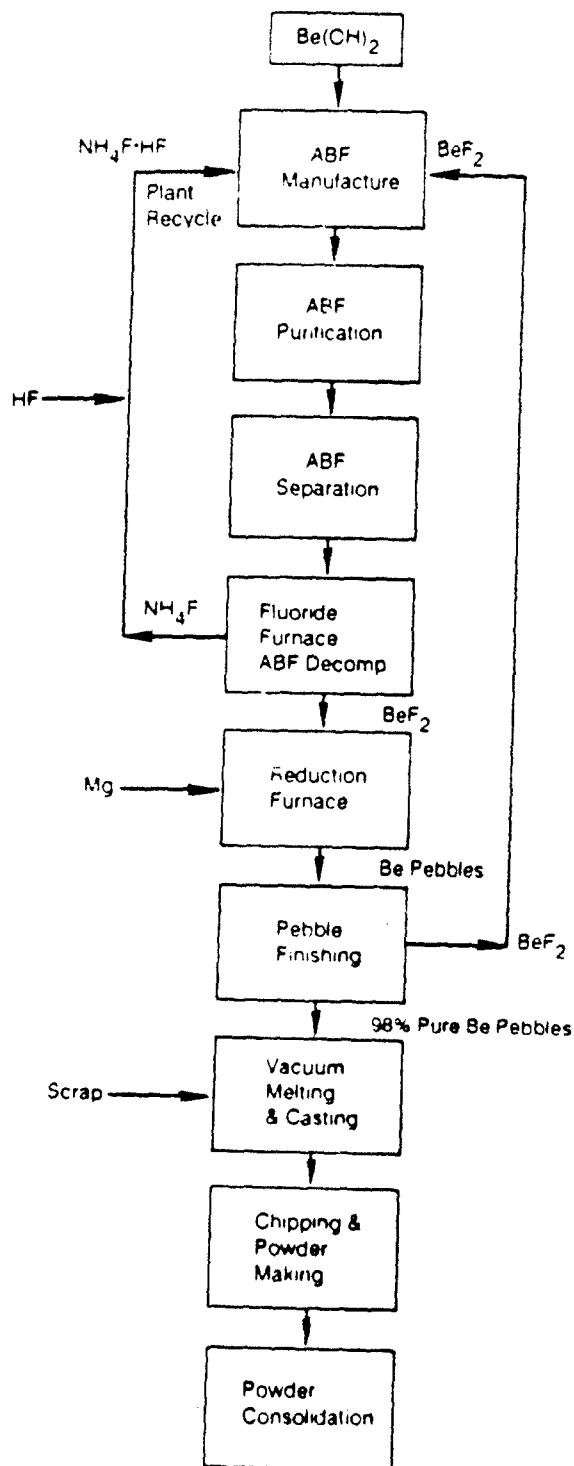
This chapter describes the existing beryllium metal production process at BWI's Elmore facility, starting with the beryllium hydroxide concentrate entering the plant and ending with the consolidation of fine beryllium powder into block (billet or slab) by vacuum hot pressing. This description is largely based on BWI reports and on the presentations made by BWI personnel to the committee (Zuehlke, 1982; Kaczynski, 1986, and oral presentation, 1988; A. Astle, oral presentation, 1988).

The process description is followed by an example of a unit process that has had problems with the generation of excessive concentrations of airborne beryllium that have led to periodic plant evacuations. To correct the major environmental problems faced in the production of beryllium metal, BWI has made a number of important changes in processing equipment, especially in recent years. Examples of some of the more critical modifications are described in this chapter.

#### EXISTING PROCESS

To a large extent, the current process for converting the beryllium hydroxide concentrate into beryllium metal and consolidating the metal into a useful engineering product has evolved from processes used in the 1940s, with changes coming about in response to the specific production problems (Zuehlke, 1982). More often than not, these problem areas have been environmental in nature. The processing route taken, after winning the metal, has been by powder metallurgy rather than the cast and wrought route because of the finer grain size achievable, which gives superior mechanical behavior to the product.

An overview of the important steps in the production process is shown in Figure 3-1. The first three production steps belong to the chemical plant operation and generally involve the mixing of chemicals in solution and the purification of these solutions by the removal of impurity precipitates through filtration. The next two operations, the decomposition of ammonium beryllium fluoride (ABF) and its subsequent reduction with magnesium, are high-temperature furnace processes that provide a greater risk of air contamination from beryllium and beryllium-containing compounds. The last three process steps are inherently problem areas because these pro-



**FIGURE 3-1** Steps in the production of consolidated beryllium.

cedures involve the handling of fine beryllium-containing powder and dust. The remainder of this section describes the process steps.

#### Manufacture of Ammonium Beryllium Fluoride

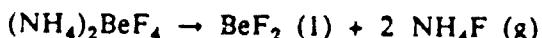
The first step in the production process is the conversion of the beryllium hydroxide ore concentrate to ABF. This reaction is carried out by mixing solutions of ammonium hydrogen fluoride with beryllium hydroxide and reacting the two to form ammonium beryllium fluoride:



The ABF is subsequently purified by a series of precipitation and filtration steps. The pH of the solution is first adjusted to 7.3 by the addition of 30 percent ammonium hydroxide, then calcium carbonate is added to the solution at 90°C, resulting in the complexing of any aluminum present by the calcium carbonate. The aluminum-containing material is removed by vacuum filters, and the filtrate is subsequently treated with lead oxide to reduce the manganese and chromium content of the solution by precipitation. These precipitates are once again removed by filtration. Finally, the filtrate is treated with ammonium sulfide to reduce the level of iron, zinc, lead, copper, nickel, and other impurity elements. The purified ABF solution is then subjected to a vacuum evaporator treatment to form ABF crystals, which are separated in a horizontal bowl centrifuge and dried.

#### Formation of Beryllium Fluoride

The purified crystals of ABF are next decomposed in an induction-heated graphite crucible furnace:



The ammonium fluoride gas (g) is captured in wet scrubbers and recycled through the process. The beryllium fluoride liquid (l) is discharged from the bottom of the furnace, where it is cooled and solidified on a water-cooled drum.

#### Production of Beryllium Pebbles From Beryllium Fluoride

The beryllium fluoride from the decomposition process is reduced with magnesium to beryllium pebble:



This exothermic reaction takes place in an induction-heated crucible furnace at approximately 900°C with magnesium concentrations of less than 70 percent of the stoichiometric requirements. The product of the reac-

tion, a mixture of beryllium, magnesium fluoride, and beryllium fluoride, is heated to 1400°C and is poured into a graphite-lined transfer pot. The pot is cooled on a continuous cooling conveyor, and the solidified product is moved to the pebble finishing operation.

#### Pebble Finishing

The first step in the pebble finishing operation is to break up the solidified product in a hammer mill. The product, consisting of a mixture of beryllium fluoride, magnesium fluoride, beryllium pebbles, and beryllium fines, is then treated in a rotary mill into which a solution is introduced to dissolve the soluble beryllium fluoride and separate out the insoluble magnesium fluoride. Further purification of the beryllium pebbles is accomplished in a sink-float operation using bromochloromethane. In this step, any residual magnesium fluoride and other impurities sink to the bottom of the medium and the beryllium pebbles, together with residual graphite, are skimmed off the top. The pebbles are then subjected to a leaching operation with a weak acetic acid solution to remove iron from the pebble surfaces. They are then sent through a magnetic separator and finally through a visual inspection station, where foreign material is manually removed. The end result is a 98 percent pure beryllium pebble product.

#### Vacuum Casting

The casting step is designed to produce vacuum-cast ingots approximately 14 in. in diameter by 36 in. long as the feedstock for the subsequent powder-making operation. The vacuum melting step also serves to homogenize the added scrap and beryllium feedstock (approximately 42 percent of the charge is pebbles and 58 percent is scrap) and to provide some purification (e.g., magnesium content is lowered). A charge, ranging from 400 to 450 lb, is vacuum-melted at 1400 to 1450°C in a crucible made of hand-rammed magnesium oxide inside a tilt-pour induction furnace. The molten beryllium is poured into a graphite mold, 14 in. in diameter by 36 in. long, and the dross is tilt-poured into a dross mold for later recycling.

In preparation for the first step in the beryllium powder-making process, the ends of the ingot are first machined down and then a  $\frac{1}{4}$ -in. layer is removed from the cylindrical surface. Finally, any dross inclusions that have become embedded in the surface are removed by hand chipping.

#### Powder Making

The first step of the beryllium powder-making process involves machining of the cast ingot using a multiple-bit gang-tool assembly. The chips

are collected, with the aid of a cyclone, into 55-gal drums, sized to smaller than 1/8 in., magnetically separated, and x-ray inspected.

The next step involves the comminution of the chips in one of three ways: attritioning, impact grinding, or ball milling. Attritioning has been the principal way of producing beryllium powder until fairly recently. Powder production by impact grinding has grown substantially in recent times and appears to be replacing attritioning as a production method. Ball milling, on the other hand, accounts for only a small portion of beryllium powder production. This method is used in producing the finer beryllium powders that are used primarily for instrument applications.

Attritioning is a grinding process that takes place between backed, slotted plates; one of these is stationary and the other rotates. An argon atmosphere minimizes oxidation. Size control is effected by screening, with the oversize chips being recycled for further grinding.

Impact grinding is carried out by injecting beryllium chips into an air stream carried through a nozzle at 450 psi and impacting them against a beryllium target. The oversize chips from this process are collected on screens and are subsequently recycled through the process.

The ball milling operation is a batch process carried out in a cylindrical mill with steel balls. The milled product is emptied into a transfer container, and the product goes from there into an air classifier for sizing. The oversize chips are remilled with additional beryllium powder (attrited or impact-ground) as input.

The products from the powder-making processes are subjected to various quality-assurance techniques, including chemical and particle size analyses, and x-ray inspection.

Various lots of beryllium powder are chosen on the basis of their chemistry and powder size characteristics. These are mixed in blenders of different sizes, ranging from 10 to 100 ft<sup>3</sup> capacity, in preparation for vacuum hot pressing. The blended lots are subjected to additional magnetic separation (at least 2 times) and are once again evaluated for their chemical content and particle size distribution. As a final step in the blending operation, the charge is screened to remove any particles greater than 0.006 in. (152 µm) to avoid an excessive high-density inclusion count. In preparation for loading into the vacuum hot press die, the powder needed for the compact is mixed in a roll blender, and then samples of the powder are radiographically inspected at least twice.

#### Vacuum Hot Pressing

The principle method by which beryllium powder is consolidated is by

vacuum hot pressing (VHP). Hot isostatic pressing (HIP) is making some inroads into this application because of its promise for near-net-shape (NNS) processing and for minimizing the amount of scrap generated (see Chapter 5 for a discussion of NNS processing).

The beryllium powder is vibratorily packed into a suitable die to a packing density of approximately 50 percent of theoretical. Graphite dies are used for hot-pressing sizes up to approximately 20 in. diameter. For larger sizes, the powder is consolidated in steel cans supported by alloy steel dies. Most VHP operations take place in double-acting presses--i.e., the pressing action takes place by means of opposing hydraulic presses on both the top and bottom of the press. Electrical resistance or induction is used to heat the die and its charge.

A typical VHP cycle involves an outgassing step at approximately 800°C. Final pressing is at 1000 to 1100°C at pressures of about 1000 to 1200 psi for graphite dies and 500 to 600 psi for the alloy steel rings. After the pressing is completed, the compact is cooled under argon to 400°C, then the furnace is unloaded and the die and its compact are cooled to room temperature. The cooled die is stripped and refurbished for further pressing operations. The vacuum-hot-pressed beryllium block is then machined into blanks, into final parts, or into logs for shipment to other machining facilities.

#### RECENT CHANGES IN BERYLLIUM PRODUCTION PROCESSES

Before the DOE-sponsored study on the optimization of beryllium production operations was conducted by BWI, many of the unit processes used in the production of beryllium metal were rated as "out of control" from an environmental standpoint and in some cases were inefficient or not easily controlled (Zuehlke, 1982; Kaczynski, 1986). As a result of the DOE-sponsored study, many changes have been made that have led to notable improvements from the environmental standpoint. A listing of unit processes and their status as of July 1986 with regard to air contamination is given in Table 3-1. This table illustrates the improvements made in several areas and the fact that several of the unit processes were in the "out-of-control" category. Since then, further improvements have been made, and currently there are only four processes that have had incidents that would put them in the "out of control" category, as shown in Table 3-2 (A. Astle, personal communications, February 18 and August 19, 1988). The high airborne beryllium concentrations associated with these operations are generally due to one-time upsets in the normal operation.

Evaluation of the processes from an environmental standpoint--i.e., whether the process is in or out of control--is based on air sampling and on whether the beryllium concentrations found exceed the daily weighted

**TABLE 3-1 Environmental Status of Beryllium Process Areas**

Continuously in Control	Formerly Out of Control, Now in Control	Out of Control (as of July 1986)
Wet plant	Fluoride furnace	Vacuum casting
Evaporator	Reduction furnace	Billet pick
Machining	Melts crusher	Attrition mill
	Die preparation	Miag classifier
	Vacuum hot pressing	Powder ball mill
	Powder preparation	Scrap reclamation
	Sheet and foil preparation	Proprietary process
	Cold pressing	

Source: Kaczynski, 1986.

average (DWA) standard of 2  $\mu\text{g}$  per cubic meter on an "actual" basis averaged over a quarterly period (see Chapter 7 for a discussion of "actual" versus "potential" beryllium concentration in the air). There may be some disagreement on whether the use of "actual" concentrations provides the best assessment of health hazard or whether "potential" concentrations are a better measure. In addition, the use of quarterly averages of DWA tends to mask shorter-duration, high-concentration excursions. Use of daily DWA ranges rather than quarterly averages would provide a better assessment of the health hazard.

**TABLE 3-2 Processes Having Recent Environmental Excursions**

Process	Date	Description of Incident
Melt crusher	End of 1986	Mechanical failure in the form of a hole in the crusher. Single incident.
Powder blending	3rd quarter 1987	Operator error in sealing the blender.
Sheet and foil	1st quarter 1986	High air count. Single incident.
Attrition mill	4th quarter 1987	Leak in vent line. Single incident.
		Mechanical and electrical failure in a newly installed system.

Source: A. Astle, personal communication, August 19, 1988.

To illustrate the types of changes made to various processes and the improvements effected thereby, one production step is discussed in detail, namely, the decomposition of ammonium beryllium fluoride (ABF). The ABF decomposition has been reported to be under environmental control with the improvements made as a result of the DOE-sponsored and follow-on studies (A. Astle, personal communications, 1988). The discussion of this process step focuses on the engineering and environmental problems, some of the steps taken to alleviate these problems areas, and the environmental impact of the changes.

#### **Decomposition of Ammonium Beryllium Fluoride**

The decomposition step of the beryllium production process described earlier is a high-temperature furnace operation that involves handling  $\text{NH}_4\text{F}$  gas and molten  $\text{BeF}_2$  salt. This decomposition process has had a troublesome operational history. It has given rise to major environmental problems within the plant, including plant evacuation; such incidents still continue. A number of changes have been made to the system over the years to reduce these environmental problems. Many of the changes have been evolutionary. However, starting with the DOE-sponsored studies, important changes have been made, and additional ones are in the planning stages. The process modifications have led to improved control, an improved plant environment, and a reduced frequency of plant evacuations.

#### ***Problem Areas***

The operational problems associated with the ABF reduction process have centered around the corrosive nature of the products and the build-up of product dust in the ducts and ventilating system. The corrosive nature of the salts makes it difficult to incorporate sensors in the equipment for remote or automatic control. Because of these limitations, it has been traditional to rely on operator observations and control of the heat input and material feed rates. It also has been necessary to remove the build-up of  $\text{NH}_4\text{F}$  formed in the duct between the furnace and scrubber by manual scraping with a rod. The process has experienced numerous furnace upsets, "puffs," and contaminant escape. Other problems associated with the ABF reduction have involved the beryllium fluoride product--its flooding of the casting wheel and its tendency to have an undesired crystal form.

#### ***Process Changes and Equipment Improvement***

To correct some of the problems identified and to minimize environmental problems, a number of changes have been made to the process and the equipment and to the nature of the feed material. Many of these changes can be classified as improvements to the ventilation and scrubber systems. Some other alterations of note include the drying of the ABF to prevent "puffs," the redesign of the transport system for the  $\text{BeF}_2$  product, and the

installation of probe rod assemblies on each of the ABF decomposition furnaces at the fume ducts to the primary scrubbers to prevent fuming, a major cause of the plant evacuations. Additional alterations involve the redesign of the cooling wheel used in the solidification of the BeF<sub>3</sub> product.

More recent changes to the ABF decomposition facility have shown great promise for process improvement (Kaczynski, 1986; A. Astle, personal communication, 1988). A new prototype furnace has been designed and built to provide the following improvements in operation:

- Decreased operating temperature. This change in operation was aimed at decreasing the corrosion of the graphite components and providing better furnace control. Variation of the induction heating generator frequency over the range from 100 to 3000 Hz has not led to the desired results.
- Increased productivity. Increased productivity has been effected by increasing the furnace power from 100 to 200 kW. The resulting production rate has increased almost in proportion to the power increase, from 55 to 100 lb per hour.
- Prevention of fume duct plugging. Better insulation, selective heating, and use of different construction materials have met with some success. There still are problems that need solution.
- Improved instrumentation. Introduction of some sensors into the equipment has led to only moderate success. In one case, an inconel-sheathed thermocouple has been installed into the graphite torpedo, but the nonuniform flow of feed material has led to inconsistencies in the temperature readings. Flow meters and draft controls also have been introduced.
- Automatic control. Movement in the direction of automatic control has taken the form of maintaining the power to the furnace at a constant level and modulating the feed rate into the equipment.

#### *Environmental Considerations*

The "actual" quarterly DWA data for the ABF reduction furnace operation at the Elmore facility have shown a dramatic decrease from 1971 through 1987, as seen in Figure 3-2 (A. Astle, personal communication, August 19, 1988). This decrease has been especially notable in the period from 1982 through 1987 and indicates a positive response to the alterations in the ABF reduction furnace system previously described. The "potential" concentrations, on the other hand, show little improvement over the time period 1978 through 1987, indicating that there still are environmental problems associated with this operation. Plant evacuations resulting from malfunctioning of the ABF

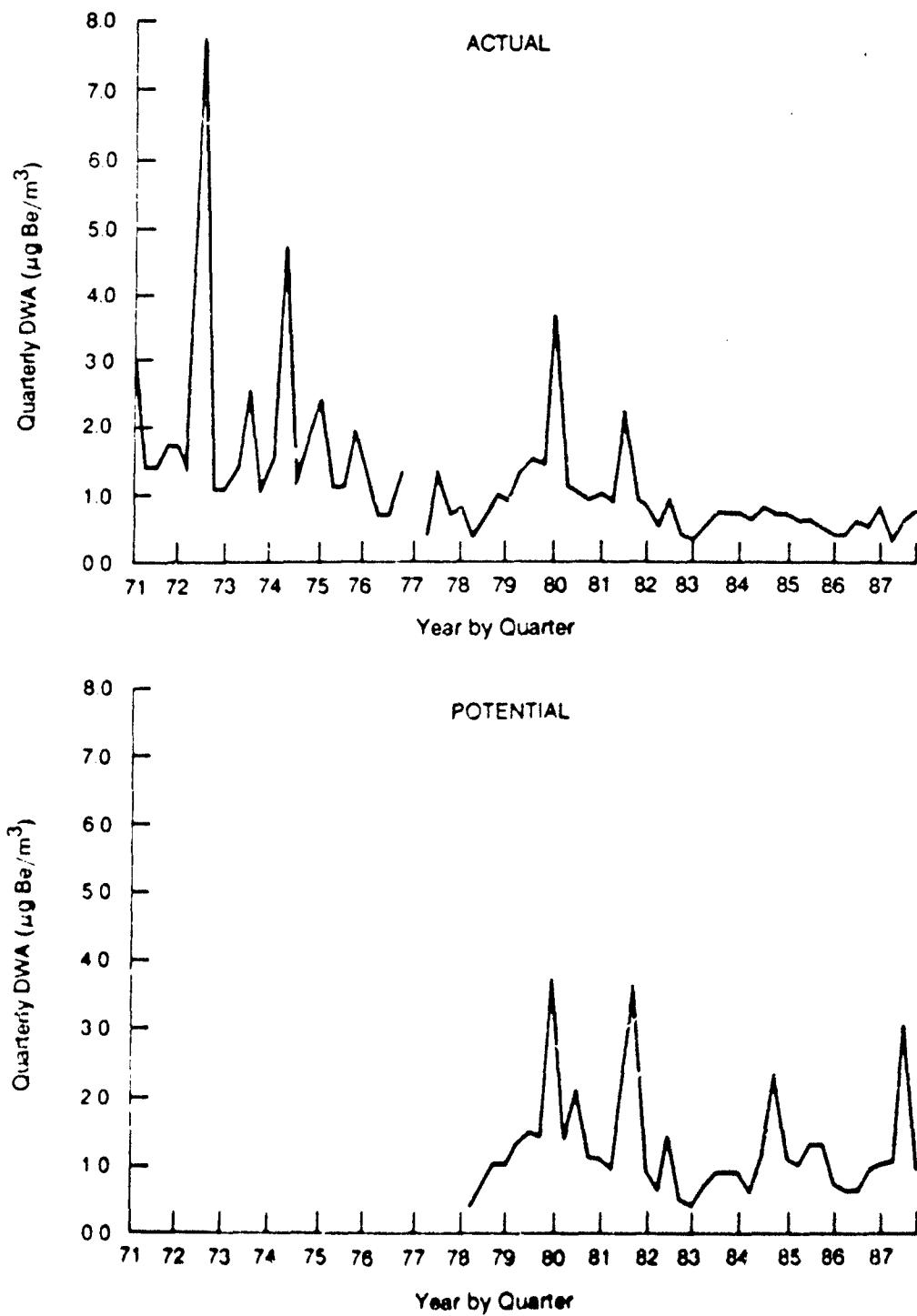


FIGURE 3-2 Airborne beryllium DWAs associated with the ABF reduction furnace operation at BWI.

reduction furnaces still occur all too often, although their frequency has decreased as a result of the changes in operation.

## CONCLUSIONS AND RECOMMENDATIONS

An overview has been provided of the existing process for producing beryllium metal. The ABF reduction process was used to show the types of problems encountered and some of the efforts that have been made to improve efficiency and minimize exposure to airborne beryllium. In spite of these efforts, which have led to great improvements, substantially more effort is required to provide an environmentally safe, efficient, in-control plant operation. This endeavor will need even greater attention if the airborne beryllium concentration parameters are made more stringent.

The following conclusions and recommendations are based on available reports, literature, and oral presentations to the committee, as well as on the committee's tour of BWI's Elmore facility.

### Conclusions

■ The overall process for the conversion of  $\text{Be}(\text{OH})_2$  to beryllium pebble is inherently sound but requires improvements to make it efficient and environmentally safe. These improvement efforts should be concentrated on those subprocesses that are the worst environmental offenders. The powder-making process, which is undergoing a major R&D effort, can benefit from some of the more revolutionary changes currently being considered--e.g., beryllium powder production by gas atomization (see Chapter 5).

■ Insufficient effort is being placed on the basic overall design of each of the production processes and the use of state-of-the-art instrumentation for process control, remote handling, and, where feasible, automated production. Most of the current processes and equipment are not well instrumented and rely on operator observations and judgment rather than remote sensing. Expertise in this area should be most beneficial.

■ More work must be conducted on understanding the basic processes on which the production methodology depends. For example, better understanding of the effect of temperature on the ABF decomposition process might lead to a lower operating temperature, resulting in milder corrosion problems. Similarly, research on the effect of stoichiometry, reaction temperature, and holding time in the magnesium reduction of  $\text{BeF}_3$  might lead to improvements in process efficiency and product morphology--i.e., the size and amounts of beryllium pebbles,  $\text{MgF}_2$ , and  $\text{BeF}_2$  produced. High-quality work is needed in support of process development so that the production parameters can be set and controlled at their optimum levels from the standpoint of efficiency and environmental safety.

- The criterion used to assess whether a process is in or out of control is inadequate. The criterion should depend on "potential" rather than "actual" airborne beryllium concentrations and should be reported as daily (or more frequent) averages rather than quarterly averages; more detail is given in Chapter 7.

#### Recommendations

- Continue to make improvements to the currently used magnesium reduction process with the goals of improving process efficiency and control and of alleviating environmental problems. Concentrate these efforts on those subprocesses that are the worst environmental offenders.
- Continue to review the overall design of each of the currently used unit processes, especially those with environmental problems. The objective of this work should be to develop new, improved processes and equipment that would be more efficient and safer by the addition of state-of-the-art sensors and automatic control. In this regard, statistical process control (trend analysis), used very successfully in other industries, should be considered. Expertise in all these areas should be sought where needed.
- Conduct process development experiments in support of the unit process design review.
- Consider the use of "potential" beryllium concentrations rather than "actual" values for the assessment of the cleanliness and safety of an operation. Daily rather than quarterly averages should be used in this assessment.

#### REFERENCES

Kaczynski, D. J. 1986. Research and Development Study for Optimization of Beryllium Production Operations, Task V, Final Report. Prepared for the U.S. Department of Energy, Contract DE-AC04-82AL18071, Brush Wellman Inc. (July).

Zuehlke, J. R. 1982. Research and Development Study for Optimization of Beryllium Production Operations, Task I Report: Review of Current Operations. Prepared for the U.S. Department of Energy, Contract DE-AC04-82AL18071, Brush Wellman Inc. (July).

## Chapter 4

# ALTERNATE METALLURGICAL EXTRATION TECHNIQUES

In this chapter, alternative and improved metallurgical extraction techniques, other than those currently employed by BWI, are discussed. The intent is to describe the state of the art of these alternatives and their potential economic and environmental impact.

### ADVANCED MAGNESIUM REDUCTION

Batch reduction of  $\text{BeF}_3$  to beryllium metal is practiced commercially, and the production of  $\text{BeF}_3$  is well established. With continued and steady improvement, it is believed that  $\text{BeF}_3$  production can be made to comply with future environmental emission standards, particularly since further improvements are anticipated in the design and control of  $\text{BeF}_3$  furnaces. Although the process is commercial, its efficiency is low, and success in efforts to improve efficiency should yield good dividends. It is believed that these efforts should be emphasized and given higher priorities than hitherto.

#### Current Performance

In the current batch reduction with magnesium metal, only about 50 percent of the beryllium charged as  $\text{BeF}_3$  is recovered as beryllium pebbles; the other 50 percent has to be recycled. For each batch reduction, the amount of magnesium charged is purposely set below the stoichiometric requirement that is needed to reduce all the  $\text{BeF}_3$  present, so that a lower-viscosity slag of  $\text{BeF}_2\text{-MgF}_2$  mixture is produced that enhances the formation of beryllium pebbles. The recovered pebbles amount to about 70 percent of the expected beryllium pebble yield, based on the amount of magnesium reductant fed into the furnace. Several possible mechanisms for yield loss are suspected. Some of the magnesium is known to be oxidized by air leakage into the furnace and thus is lost to the reduction reaction. Also, part of the beryllium produced is in the form of metal fines entrapped in the  $\text{BeF}_2\text{-MgF}_2$  slag and forms no pebbles. In addition, the high viscosity of the slag may cause poor pebble formation and yield. Thus, the following programs to improve efficiency have been suggested, some of which are currently under study (Kaczynski, 1986a, 1986b):

1. Reduction under inert atmosphere;
2. Addition of a third salt to lower viscosity of slag;
3. Continuous or semicontinuous operation using a tall reactor; and
4. Improved instrumentation and equipment leading to totally enclosed or remote operation.

These suggestions are discussed in the following paragraphs.

#### *Reduction Under Inert Atmosphere*

Reduction under inert atmosphere should be highly beneficial by eliminating oxidation, whether of magnesium or beryllium, thereby improving the yield. Any improvement in yield should result in reduced processing cost. Furthermore, the absence of magnesium oxide may have a beneficial effect on the viscosity of the slag and may also prolong furnace life. Priority should be given to implementing this suggestion on the commercial scale.

#### *Addition of Third Salt*

Addition of a third salt also may have a beneficial effect but could introduce undesirable complications, particularly in the separation and possibly recycling of the third salt. Although many salts could be used, practical serious considerations narrow the choices to NaCl or NaF. Bench-scale experiments involving systems of MgF<sub>2</sub>, BeF<sub>2</sub>, and NaF or NaCl are needed to determine any potential advantage from adding a third salt and any disadvantage in its subsequent separation. Limited information on salt mixtures is available in the literature (Braunstein et al., 1971). If test results prove promising, a conceptional process for the separation and recycling of the third salt would then have to be worked out. An evaluation of the possible yield gain versus increased complexity needs to be made before additional efforts in this area can be justified.

#### *Continuous or Semicontinuous Operation*

The tall reactor is only in the preliminary conceptional stage, and no pilot plant testing has been conducted. However, the feeding of molten magnesium and molten BeF<sub>2</sub> may be gradually tested even for the present batch reduction furnaces. Full development of the tall reactor and continuous operation is believed to be quite expensive; development costs may run into the multimillion-dollar range and involve a development effort on the order of a decade. Eventually, as the market for beryllium expands, this approach, as well as the continuous production of BeF<sub>2</sub>, could generate serious interest.

#### *Improved Instrumentation and Equipment*

As will be discussed in Chapter 7, current beryllium exposure data are

insufficient to permit setting a maximum safe personnel exposure standard for beryllium or its compounds. It is thus conservative and prudent to attempt to achieve the best possible emission control that provides the lowest personnel exposure. Improved instrumentation and better-engineered equipment, as well as thorough operator education and training, will permit the beryllium pebble plant to be operated to meet environmental regulations. A stepwise approach is probably the preferred and more constructive strategy to apply here, which could lead eventually to remotely operated and totally enclosed systems. Specifically, the following recommendations are offered:

- Improve instrumentation for the reduction furnaces to permit control of process variables so as to obtain the best yield of pebbles and to prevent possible "blow-offs" during reduction.
- Design new, better-engineered, larger-capacity reduction furnaces with automated charging and take-away arrangements to allow for remote operation in totally enclosed systems.
- Develop an improved method of pebble inspection that minimizes personnel handling and exposure.

#### **Environmental and Cost Considerations**

Magnesium reduction, including the wet plant for converting BeO to  $\text{BeF}_2$ , is believed to be capable of meeting any future environmental standards. Stepwise improvement, as is currently practiced in the commercial plant at BWI, should continue. As in any processing step, operators' education and training and their care and diligence to the operation are keys to good environmental personnel protection.

Any improvement in yield reduces the amount of material to be recycled. If recycling can be reduced accordingly, the processing cost can be reduced significantly (Walsh, 1983).

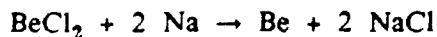
#### **SODIUM REDUCTION**

This discussion on the use of sodium reduction of  $\text{BeCl}_2$  is a conceptual examination of such a process to evaluate the merits of its applicability.

##### **State of the Art**

The ease with which molten sodium can be handled, and its modest price, availability, and high purity make sodium an important industrial reagent. It is used in the Kroll process to produce titanium and zirconium metals from their respective chlorides. Laboratory studies have indicated its applicability to produce beryllium from  $\text{BeCl}_2$ , but no commercial operations

have followed. The chemistry involved is



Sodium, from a thermodynamic perspective, also can be used to reduce  $\text{BeF}_2$  to beryllium. BWI evaluated this possibility and concluded that the disadvantages outweigh the advantages (Schow, 1983). Specifically, BWI reports that the  $\text{NaF}$  coproduct has a low vapor pressure and cannot be vaporized away from the beryllium. BWI also cites the literature and states that the very fine metal product produced by this reaction did not allow leaching in the product-separation step. However, it should be noted that BWI did not conduct bench-scale trials to support this analysis.

The most applicable literature describing the preparation of beryllium by the sodium reduction of  $\text{BeCl}_2$  dates back to the period from 1967 to 1970 (Block et al., 1968; Campbell et al., 1970). The key features of the process entail the following:

- Production of  $\text{BeCl}_2$  from  $\text{BeO}$  using chlorine and carbon at 850 to 900°C (see also the discussion of the modified Hall process). Yield of chloride from  $\text{BeO}$  was 90 to 94 percent.
- Purification of  $\text{BeCl}_2$  by vacuum sublimation, and possibly fused salt scrubbing of the vapors, at 340°C and 10 to 40 torr, with 90 to 97 percent yields.
- Reaction of vaporized  $\text{BeCl}_2$  with excess molten sodium (about 15 percent excess) at 650 to 750°C to form a beryllium sponge.
- Purification of the beryllium sponge from excess sodium and the salt by vacuum distillation of the salt at 950°C and less than 0.01 torr. Reduction and purification yields based on purified  $\text{BeCl}_2$  were between 90 and 93 percent.
- Ball milling of the beryllium sponge to a powder.
- Forming billets by CIP, HIP, and combinations of these.

Laboratory evaluation of this process also was part of the BWI Task II work plan, but the company was unsuccessful in preparing adequate quantities of  $\text{BeCl}_2$  to conduct the necessary tests.

#### Potential for Commercial Utilization

The key questions to ask about any new beryllium technology are whether it offers greater safety and improved economics, what the time frame is, and what associated costs are needed for its development. An additional

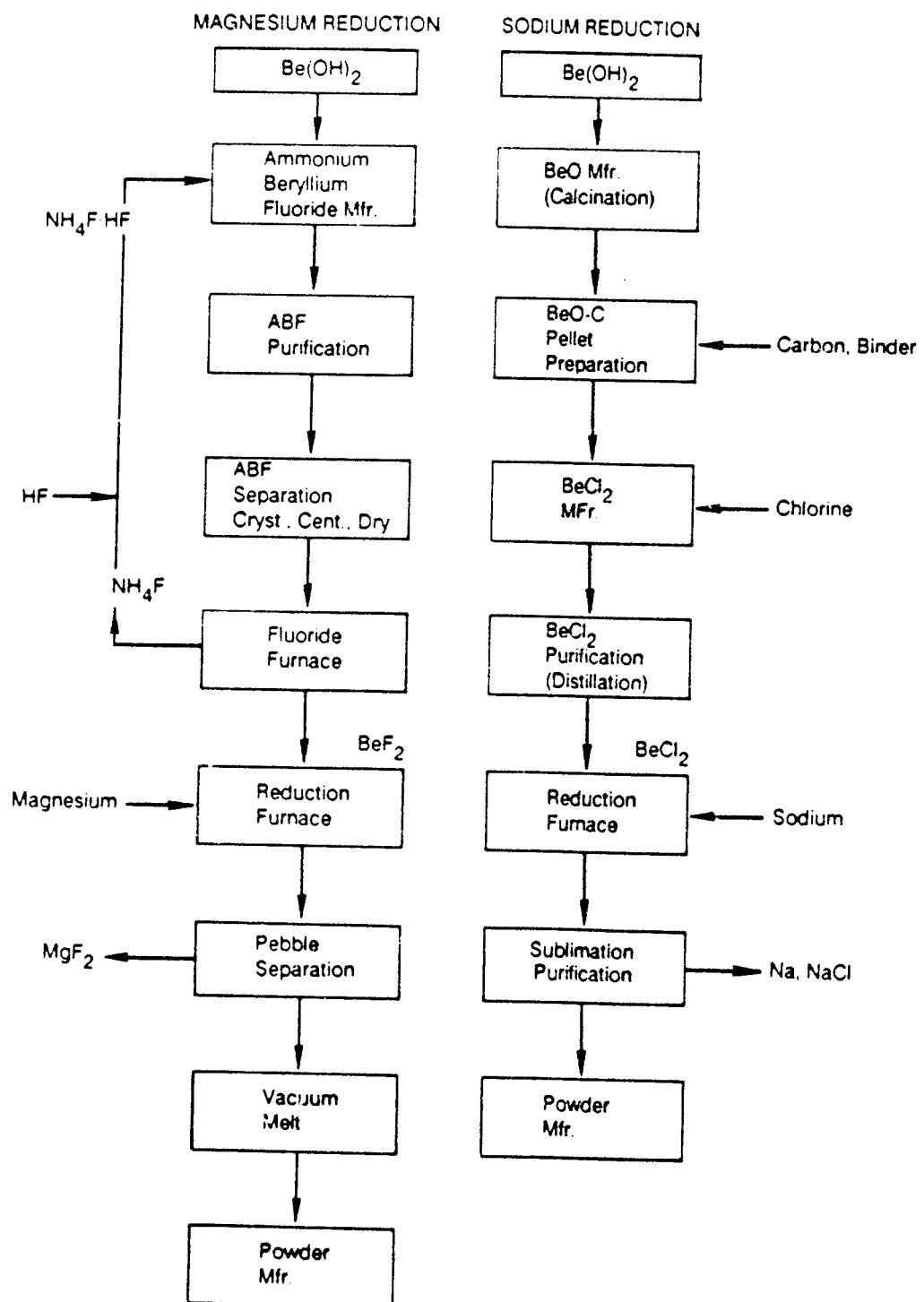


Figure 4-1 Comparison of reduction routes.

question to be posed is whether electrowinning is superior to sodium reduction once pure  $\text{BeCl}_2$  is in hand. Electrowinning was once commercially practiced and is discussed later in this chapter.

Figure 4-1 presents a side-by-side comparison of the sodium reduction route and the current BWI process. From a plant safety consideration, the  $\text{BeCl}_2$ -sodium reduction route appears to be the more hazardous, since  $\text{BeCl}_2$  is produced as a vapor and is purified as a vapor. In the current magnesium reduction route of  $\text{BeF}_2$ , the  $\text{BeF}_2$  is much less volatile and is processed as a solid or liquid of low volatility.

**TABLE 4-1 Comparison of Operating Costs: Sodium Reduction of  $\text{BeCl}_2$  to Produce Metallic Beryllium Versus Current  $\text{BeF}_2$  Route**

Factor	Na/Sponge <sup>a</sup>	Mg/Pebbles <sup>b</sup>
Engineering yield	94.1%	91.5%
Operating Costs		
Total labor + fringe	\$ 4.22	\$ 5.92
Chemicals	0.10	6.64
Magnesium	--	7.22
Sodium <sup>c</sup>	4.83	--
Chlorine <sup>c</sup>	0.72	--
Petroleum coke	0.55	--
Other operating supplies	0.59	1.67
Furnace rebuild	--	5.24
Cell rebuild	0.88	--
Utilities	2.00	4.30
Maintenance	3.10	5.24
Laboratory service	0.44	1.27
Total operating costs	\$17.43	\$37.50

<sup>a</sup>Theoretical

<sup>b</sup>Actual

<sup>c</sup>Assumes that salt by-product recovery to Na and  $\text{Cl}_2$  by sodium cell technology will not affect costs appreciably.

Source: BWI Task II Report.

From an economic viewpoint, a BWI evaluation attempted to compare the sodium reduction of  $\text{BeCl}_2$  with the current practice. BWI arrived at an operating cost differential of \$20 per pound:

	<u>Na/Sponge</u>	<u>Mg/Pebbles</u>	<u>Difference</u>
Operating cost, \$/lb	17.43	37.50	20.07

Details are given in Table 4-1. It should be understood, however, that this compares a theoretical (on paper) sodium process with a practiced magnesium technology. The BWI design of the sodium reduction route appears oversimplified, and it is doubtful that this large a differential can be attained. From a purely stoichiometric raw material viewpoint, the difference in cost of the primary reagents is only \$0.92/lb, as shown in Table 4-2. The reality, no doubt, is somewhere between these extremes.

Development of the sodium reduction technology would best be performed by a company already practicing Kroll technology, or with the assistance of such a company. Without this knowledge base, start-up would present a formidable array of problems. Other than the manufacture and purification of  $\text{BeCl}_2$ , the key difficulties seem to be control of the reduction process to prevent sodium from getting into the vapor and avoiding the formation of beryllium fines, which are difficult to recover. The production of a readily manageable beryllium sponge is desired, which allows for easy recovery and subsequent purification. An additional problem would be the identification of suitable materials for reactor construction, and another would be the cleanup and disposal of the beryllium-contaminated by-product salt,  $\text{NaCl}$ .

TABLE 4-2 Stoichiometric Key Reagent Costs

Process	Reagent	Moles/ Mole	Lb/lb	Price/lb Reagent	Cost/lb Beryllium
$\text{Mg-BeF}_2$	Mg	1	2.7	\$0.83	\$2.24
	HF	2	4.4	0.69	<u>3.04</u>
				Subtotal	\$5.28
$\text{Na-BeCl}_2$	Na	2	5.1	0.70	\$3.57
	$\text{Cl}_2$	1	7.9	0.10	<u>0.79</u>
				Subtotal	\$4.36

\*Prices from May 2, 1988, Chemical Marketing Reporter.

The time and costs required to develop the process and the containment technology needed for the  $\text{BeCl}_2$  and sodium reduction processes are estimated to be on the order of 10 years and at a cost of some \$50 million; these figures make it difficult to justify a change to an alternate technology.

## ELECTROWINNING

An examination was made of the possibility of direct electrolytic reduction of metallic beryllium from a soluble beryllium salt in an appropriate electrolyte. Such a process, if developed, would offer advantages over currently used processes, which present difficulties in their ultimate control.

### State of the Art

The state-of-the-art commercial process for the production of metallic beryllium involves the metallothermic reduction of  $\text{BeF}_2$ . The primary compounds produced by ore beneficiation and processing are  $\text{Be}(\text{OH})_2$  or  $\text{BeO}$ . These are converted to  $\text{BeF}_2$ , which is reduced to beryllium metal by reaction with metallic magnesium. Substituting  $\text{BeCl}_2$  for  $\text{BeF}_2$  and sodium for magnesium are possible process variations, as described earlier. Since both of these metallic reductants are produced electrolytically, the potential economic and environmental advantage of a one-step electrolytic process from the oxide to the metal is apparent. Such a process has been sought since the early 1930s. Even if a one-step process were not possible, the replacement of the metallothermic reduction step of the currently produced  $\text{BeF}_2$ , or alternately  $\text{BeCl}_2$ , by electrolytic reduction might still show a significant economic and environmental advantage.

The most advantageous manifestation of this approach would be a direct analogue of the Hall process used in the production of aluminum. In this process, alumina is dissolved in a molten salt electrolyte of the fluorides of aluminum and sodium (cryolite) and electrolytically decomposed (using a carbon anode) to molten aluminum and  $\text{CO}_2$  (Mitsui, 1982). The latter can be safely released into the atmosphere after removal of any residual fluoride compounds.

An immediate problem in operating such a process for beryllium is the much higher melting point of beryllium,  $1287^\circ\text{C}$  as compared to  $660^\circ\text{C}$  for aluminum. This makes removal of molten beryllium from the reduction cell difficult, if not impossible, because of the high vapor pressure of the  $\text{BeF}_2$  at so high a temperature. Problems with materials of construction also exist at that temperature, especially in such a corrosive fluoride environment. There is also no known salt system that has a  $\text{BeO}$  solubility approaching that of alumina in cryolite. Such difficulties became appar-

ent to the investigators at the Siemens Company in Germany in the 1930s, when they attempted to commercialize a high-temperature molten salt process for the electrolytic deposition of solid beryllium, and were the reasons for its abandonment (Wong et al., 1969; Illig et al., 1932). If an electrolytic process for the direct decomposition of BeO were to be developed, a significant modification of the Hall process would be necessary.

#### Modified Hall Processes

To obtain easily removable, electrolytically deposited, and well-coalesced solid beryllium metal from a molten salt solution containing BeO, the electrolyte must have

1. Adequate electrical conductivity at the necessary BeO concentration and desired temperature;
2. Sufficient solubility and solution kinetics to maintain the concentration of BeO required at the working interface, to permit an economic current density;
3. Low vapor pressure at operating temperature; and
4. Low reactivity with beryllium metal at the temperature necessary for good metal coalescence.

The U.S. Bureau of Mines conducted extensive bench-scale experiments in search of such an electrolyte in the 1960s (Wong et al., 1969; Wong, 1972). Researchers systematically studied fluoride salts and found no BeO-bearing composition of these salts from which beryllium metal could be electrolytically produced in the absence of  $\text{BeF}_2$ . Of the compositions investigated, BeO-containing solutions of LiF and  $\text{BeF}_2$ , with or without  $\text{BaF}_2$ , gave the most promising results for the electrolytic production of beryllium metal directly from the BeO. The initial cathodic deposit of such a system consisted of fine metal crystals and entrapped electrolyte. To obtain metal coalescence and subsequent efficient collection of the beryllium from this deposit, it was necessary to heat it under a molten salt cover to a temperature above the melting point of the metal. The temperature had to be held for a time and then allowed to cool to 900°C, a temperature well below the melting point of the metal and well above the melting point of the salt. This allowed easy metal separation by pouring through a stainless steel screen. The two-step process could be carried out in a single cell as a batch process by varying the temperature of the electrolyte in a vessel designed to tilt and pour. Alternatively, it could be a semicontinuous process where the cell is held at operating temperature while removable cathodes are periodically stripped and the deposit separated from the metal in a second vessel (Wong et al., 1969; Wong, 1972).

From this work, a bench-scale process was developed and demonstrated but never commercialized. The process operated at 700°C and 2.6 V, using 60 mol percent LiF and 40 mol percent BeF<sub>2</sub> electrolyte. The major problem encountered was the limited solubility of BeO (0.09 mols of BeO per kilogram of electrolyte at operating temperature), which restricted the passage of current at voltages low enough to avoid fluorine gas production at the anode. Increased anode area, through geometric configuration or porosity, and feeding the BeO close to the anode may allow economic current densities, but more research and development would be needed to determine this.

Such a process seems feasible, but it may offer little economic or environmental advantage over the present process since, if this is to be a continuous semiclosed process, a second step for coalescence and filtration for metal collection would be necessary. This step, with its extensive open handling of a molten BeF<sub>2</sub>-containing salt, may be economically and environmentally no better than the BeF<sub>2</sub> production step in the present process. An electrolytic cell, which must be opened to remove the cathodes to collect the product deposit, also may be no better environmentally than the present metallocermic reduction reactor.

Another modification of the Hall process is similar to the Bureau of Mines process described. In this process, a 60 mol percent LiF and 40 mol percent BeF<sub>2</sub> electrolyte saturated with BeO is used, but the beryllium metal is deposited on a solid copper cathode at an operating temperature below the melting point of beryllium but above the melting point of certain beryllium-copper alloys, 900 to 1000°C. When beryllium is deposited on the copper cathode, it forms a low-melting alloy locally that drips off the cathode. The molten alloy collects on the cell bottom, where it can be vacuum-tapped, as in aluminum production at about the same temperature. This is a feasible way to make master alloys, but it is more costly than the current arc furnace production. If pure beryllium metal is desired, a means of separating beryllium from the copper must be found. Vacuum distillation has been suggested, at pressures between 10<sup>-3</sup> and 10<sup>-6</sup> atmospheres, because the boiling points of the metals are only 25 to 45°C apart at distillation temperatures of between 1200 and 1500°C. Such a process would give difficulties in materials of construction and require close control of condensation temperatures and perhaps would require multiple condensation stages to obtain satisfactory separation. The high vapor pressure of BeF<sub>2</sub> at the high operating temperature of the cell also could present problems.

This process is intriguing and could be pursued if alloy production is desired. To produce pure beryllium, however, even if it were possible, would require a great deal of development effort, with the attendant high costs for process research under extreme operating conditions. This effort, even if successful, would require an investment that cannot be justified based on the projected market for pure beryllium (Zuehlke, 1983).

A third possible Hall process modification was investigated at BWI (Kaczynski, 1986c). It is based on the Pora process for aluminum production that was demonstrated to be technically sound on bench-scale work but never commercialized (Withers and Upperman, 1982; VAW, 1982; Zuehlke, 1983). The process produces aluminum directly from alumina and carbon, using an electrolyte of an  $\text{AlCl}_3$ -bearing solution of lithium and sodium chlorides;  $\text{CO}_2$ , instead of the expected chlorine, is evolved at that anode. This is accomplished by adding the alumina continuously as an integral part of the anode. The anode is made, in stoichiometric ratio for aluminum production, of 2.0 lb of alumina to 0.5 lb of carbon equivalent as coke and pitch binder. By having alumina and carbon in close proximity and at proper reaction ratio, the chlorine anode product from electrolytic decomposition of the  $\text{AlCl}_3$  in solution never appears as such but reacts through a charge transfer with the carbon and the alumina at the anode to produce  $\text{AlCl}_3$  and  $\text{CO}_2$ . The  $\text{AlCl}_3$  goes into solution to maintain the proper  $\text{AlCl}_3$  concentration, and  $\text{CO}_2$  goes off as a relatively innocuous gas.

The beryllium analogue of this process would use BeO-carbon composite anodes and a low-melting chloride electrolyte such as lithium chloride-potassium chloride eutectic. Beryllium chloride would be decomposed electrolytically to produce beryllium metal at the cathode and  $\text{BeCl}_2$  and  $\text{CO}_2$  at the anode through reaction of the carbon and BeO with the chlorine through a charge transfer. Experiments conducted by BWI (Kaczynski, 1986c) showed that the reaction at the anode was too slow, if it took place at all, for a reasonable production rate, and, although  $\text{BeCl}_2$  was readily decomposed, unlike the Pora process for aluminum, only chlorine was evolved at the anode.

Recent experiments by J. C. Withers, the developer of the Pora process, reported success in the production of magnesium by an analogous method only when he used a solution of both fluorides and chlorides. This indicates that the beryllium analogue might be successful if a proper mix of chlorides and fluorides could be found. However, this is a possibility that remains to be demonstrated. Even if successful, the process requires the manufacture and baking of anodes that contain BeO, which may be as difficult to contain environmentally as the production of  $\text{BeF}_2$  that it would replace.

#### Degussa Process

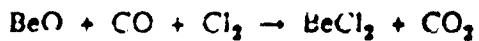
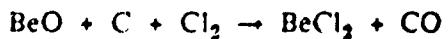
In the Degussa process, beryllium metal is produced by the electrolytic decomposition of  $\text{BeCl}_2$  dissolved in a solution of molten chlorides. The operating temperature permits depositing the metal as solid flake. Unlike the possibly alternate processes previously discussed, this process was commercialized, having been successfully operated in Germany in World War II and in France and England after the war. The process must have been economically competitive and environmentally satisfactory in its day.

It was even reported in one instance in the literature as less costly, easier to operate, producing a purer product, and having fewer environmental problems than the process in operation at BWI today (Kaczynski, 1986d). Few details were available in the literature, and what could be found was insufficient to permit a careful economic and environmental analysis for comparison with the present operation. To gather some necessary data, a demonstration model was constructed and operated at BWI.

An inherent flaw in the process is that it does not fulfill the original desire for a one-step process that goes from BeO to beryllium metal. It simply replaces the electrolytic production of the metallic reductants (magnesium or sodium) with a similar electrolytic production of beryllium. It also replaces the metallothermic reactor in the present process with a reactor for the production of BeCl<sub>2</sub> before the electrolytic step. Since the number of operations remains the same, advantages over the present process can only exist in higher output efficiencies, characteristics that make it less labor-intensive with attendant less exposure, or simpler design problems for total enclosure. In fact, none of these favorable differences is apparent, since the original operation was a batch process. It involves many hand-operated steps for removal and purification of the beryllium flake, and production of the BeCl<sub>2</sub> it uses is every bit as difficult to operate as the current metallothermic reactor.

Successful operation of the demonstration unit permitted optimization of the process at 350°C, at 40 to 58 weight percent BeCl<sub>2</sub> in NaCl and a 4-in. anode-to-cathode distance. Optimum current density depended on the means of product collection, since it controlled the morphology of the deposit. Between 20 and 60 amp/ft<sup>2</sup>, it was far under the production rates of the major electrolytic processes of aluminum, magnesium, and chlor-alkali, which are an order of magnitude higher. Anode-to-cathode distances, which control the number of kilowatts expended per pound of product, are normally less than half the optimum determined for this process.

No effort was made to demonstrate a feasible reactor to produce BeCl<sub>2</sub> seed for the electrolytic reduction. However, the assumption appears reasonable that chlorination of a fluid bed of calcined BeO in the presence of solid carbon (petroleum coke) or CO gas can apply, based on the full-scale commercialization of a totally enclosed similar reactor for the production of AlCl<sub>3</sub> by the Aluminum Company of America at Anderson County, Texas. The reactions are as follows:



The toxicity of BeO, however, introduces a dimension not present in AlCl<sub>3</sub> production. If CO were used as the reactant, a temperature of 900°C

would be needed, and this introduces another costly step involving a hazardous material. If the cheaper coke were used, the CO<sub>2</sub> leaving the system would have to be carefully scrubbed to remove PCBs generated when solid carbon is used. Adsorbed PCBs on the product could be an additional hazard when it is volatilized as the BeCl<sub>2</sub> is fed into the molten electrolyte. All of these problems were solved by a total closed-loop enclosure of the process used by Alcoa, but there is argument in favor of solving the environmental problems of the present BWI process rather than embarking on an extended development program with many possible unknowns.

Beryllium chloride was produced commercially in the 1950s in Europe, but the process as practiced then is believed unsuitable for today's environmental protection and personnel exposure requirements.

#### Other Alternate Processes

Electrowinning from organic solutions and the use of a mercury cathode to facilitate the removal of solid beryllium deposits as an amalgam in the Bureau of Mines process have been suggested in the literature or in patents. In the former case, no satisfactory organic solution has been found that contains beryllium compounds with sufficient electrical conductivity to permit an electrolytic process. As for mercury cathodes, they have been successfully used commercially in chloralkali production, but in conjunction with aqueous electrolytes at low temperatures where mercury vapor pressure is low. Certainly, at the higher temperatures necessary for beryllium production, the lowered environmental problems gained through ease of product removal in a continuous process would be more than offset by the separation process involving mercury vapors that may be an even greater health hazard.

### ELECTROREFINING

The electrorefining process is a technique that has been used to obtain high-purity beryllium metal from a lesser grade of metal. Unlike electrowinning, the beryllium feed material is already in metal form but contains excessive amounts of impurities that cannot be tolerated for certain specific applications. In the electrorefining cell, beryllium metal, as well as the metallic impurities, become dissolved in a fused-salt electrolyte. The valuable beryllium metal ions selectively migrate to and are collected at the cathode in the form of plate-like crystals. When removed from the cell, these metal crystals can be consolidated into a more processible metal form.

#### Laboratory Experimentation

Early investigations were undertaken by several researchers shortly

after World War II (Gurklis et al., 1952). These early results were expanded by U.S. Bureau of Mines experimenters, who had developed electrolytic techniques for preparing titanium (Nettle et al., 1957), vanadium, chromium, zirconium, and hafnium (Blue and Baker, 1958). Thin, plate-like crystals of beryllium metal were produced by electrolyzing technical-grade beryllium metal beads of about 94 percent purity, as a soluble anode in a mixed chloride electrolyte containing potassium, lithium, and beryllium chloride salts (Wong et al., 1960). Analysis of the final electrorefined beryllium product formed at the cathode revealed that it contained a marked reduction in impurities from those initially present in the feed metal.

These initial results were expanded subsequently to determine how various operating conditions would affect the ultimate purity of this metal product (Wong et al., 1962). The electrolyte composition contained 50 to 55 percent LiCl, 35 to 40 percent KCl, and 3 to 16 percent BeCl<sub>2</sub>, at temperatures between 450 and 550°C. Beryllium metal, with extremely low oxygen and metallic impurities, was prepared in this electrolyte. Oxygen in the anode feed was reduced from 3.27 percent to approximately 0.04 percent in the refined metal, and magnesium frequently was reduced from 2.66 percent to as low as or less than 0.0003 percent. In addition, aluminum, nickel, chromium, and cobalt were reduced to an amount almost undetectable by spectrochemical analysis; iron and silicon were substantially reduced; and a lesser degree of reduction was indicated for manganese, copper, and probably calcium.

Initial studies were conducted in a 4-in.-diameter mild-steel electrorefining cell; these were expanded to a cell 12 in. in diameter and eventually to a prototype cell 31 in. wide, 15 in. long, and 27 in. high. Operation of the prototype cell for 2 years was believed to have demonstrated that adapting the electrorefining process to an enlarged scale of operation presented few difficulties in mechanical functions, maintenance of optimum operating conditions, and control of product purity. However, it must be emphasized that this experimentation was not representative of any production-scale operation. The U.S. Bureau of Mines developed operating cost data for electrorefining beryllium in the prototype cell. These data are given in Tables 4-3 and 4-4 (Wong and Klosterman, 1964).

#### Commercialization

In the early 1970s Kawecki Berylco Inc. (KBI) established a beryllium electrorefining facility using the laboratory technology developed by the U.S. Bureau of Mines (Pistole, 1983) as well as the commercial technology used earlier by Pechiney and General Astrometals Corporation. Pechiney had previously sold beryllium flake on the world market for several years. The technology was subsequently transferred to General Astrometals Corporation in the United States and later to Kawecki Berylco Inc. when it purchased the General Astrometals processing and fabrication facilities.

TABLE 4-3 Cost of Electrolyte (1964)<sup>a,b</sup>

Item	Cost
Labor (actual working time)	
Mixing, loading, and drying LiCl and KCl, man-hours	16
Reacting Be metal with Cl <sub>2</sub> , man-hours	98
Total man-hours	114
114 man-hours at \$3.06/man-hour	\$348.84
Electricity (heating cell)	
Drying LiCl and KCl and heating to 500°C, kWh	658
Reacting Be metal with Cl <sub>2</sub> , kWh	<u>628</u>
Total kWh	1286
1286 kWh at \$0.005/kWh	6.43
Water (cooling cell parts)	
Drying LiCl and KCl and heating to 500°C, gal	47,300
Reacting Be metal with Cl <sub>2</sub> , gal	<u>32,640</u>
Total gal	79,940
79,940 gal at \$0.11/1000 gal	8.79
Helium (cell inert atmosphere)	
Reacting Be metal with Cl <sub>2</sub> , cu ft	149
149 cu ft at \$0.043/cu ft	6.41
Materials:	
KCl, 189.5 lb at \$0.40/lb	\$ 75.80
LiCl, 155.5 lb at \$0.95/lb	147.3
Cl <sub>2</sub> , 56.0 lb at \$0.15/lb	8.40
Be metal <sup>c</sup> , 7.34 lb at \$50/lb	<u>367.00</u>
Total cost of materials	\$598.93
	<u>598.93</u>
Total cost for 408.1 lb of electrolyte	\$969.40
Cost per pound of electrolyte (\$969.40/408.1 lb)	\$ 2.38

<sup>a</sup>On the basis of preparing 408.1 lb of electrolyte with the composition of 52.4 mol-percent LiCl, 36.3 mol-percent KCl, and 11.3 mol-percent BeCl<sub>2</sub>.

<sup>b</sup>Not including capital, overhead, and supervision costs.

<sup>c</sup>Beryllium beads, 97 percent pure.

TABLE 4-4 Operating Cost per Pound of Electrorefined Beryllium (1964)<sup>a</sup>

Item	Cost
Labor (actual working time)	
Operating cell, man-hours	1.93
Leaching product <sup>b</sup> , man-hours	2.49
Repairs, cleanup, etc., man-hours	0.22
Total man-hours	4.64
4.64 man-hours at \$3.06/man-hour	\$14.20
Electrolyte dragout	
With cathode, lb	1.908
With anode residue, lb	1.636
Total lb	3.544
3.544 lb at \$2.38/lb	8.43
Electricity	
Heating cell, kWh	226.4
Electrolysis, kWh	6.8
Total, kWh	233.2
233.2 kWh at \$0.005/kWh	1.17
Water (cooling cell parts): 13,660 gal at \$0.11/1000 gal	1.50
Helium: 10.6 cu ft at \$10.4/240-cu-ft cylinder	0.46
Materials for leaching and cleaning	
Nitric acid, 1.053 lb at \$0.20/lb	\$0.21
Demineralized water, 15.9 gal at \$20/1000 gal	0.32
Acetone, 0.733 lb at 36/lb	0.26
Hydrochloric acid <sup>c</sup> , 0.471 lb at \$0.173/lb	0.08
Total cost of materials	0.87
Operating cost per pound of electrorefined beryllium metal	\$26.63

<sup>a</sup>Not including capital, overhead, supervision, and anode feed costs.<sup>b</sup>Based on leaching product in 0.415-lb (1 deposit) batches; cost for this item can be greatly reduced in a large-scale operation.<sup>c</sup>Used in cleaning cathodes and anode baskets.

KBI's beryllium electrorefining process consisted of the electrolysis of impure beryllium in a 3-salt electrolyte consisting of KCl (48 weight percent), LiCl (37 weight percent), and BeCl<sub>2</sub> (15 weight percent) at 500 to 570°C. The process produced beryllium deposited on a nickel cathode in the form of dendrites or flakes. Purity of the electrorefined beryllium obtained averaged 99.92 percent. A list of typical impurities is shown in Table 4-5.

Two types of electrolytic cells, known as standard and solid anode cells, were developed to process beryllium scrap in the form of loose beryllium chunks and pressed solid cylinders. These cells were operated from 1970 through 1979. Toward the end of the period, daily production quantities averaged 30 pounds or approximately 1,000 pounds of electro-refined beryllium metal per month. No cost data were available for these activities.

Further experimentation on the electrorefining of beryllium metal was undertaken starting in March 1981 by researchers at the Rocky Flats plant of Rockwell International (Mitchell et al., 1987). Scrap beryllium metal was purified by the electrorefining technology developed by Cabot Berylco, Inc., and adapted by Rocky Flats personnel. Beryllium metal flake product was produced with a purity greater than 99.95 percent at a direct operating cost of \$489.00 per pound; over 80 percent of the direct cost of production is manpower. The studies led to the development of a half-scale demonstration cell, which was operated in late September 1987 for a period of 1 week.

As in previous studies, the electrolyte continued to be a salt mixture of KCl, LiCl, and BeCl<sub>2</sub> (50:40:10 weight percent) held at approximately 500°C. Up to 16 lb per day of beryllium metal was produced. As the age of the cell increases, the amount of beryllium flake produced decreases.

TABLE 4-5 Average Impurities of the Electrorefined Beryllium Metal

Impurity	Amount	Impurity	Amount
BeO	0.4%	Fe	80 ppm
C	0.01%	Si	10 ppm
Ni	50 ppm	Mg	30 ppm
Mn	8 ppm	Ag	5 ppm
Pb	5 ppm	Al	20 ppm
Cr	15 ppm	Cu	20 ppm
Cl	450 ppm	CO	5 ppm
Mo	10 ppm	Zn	100 ppm

because of the buildup of BeO in the electrolyte. The oxide was produced by water vapor entering the cell and reacting with  $\text{BeCl}_2$ . This is believed to be a slow deterioration process. Average analysis of five electrolytic runs showed a reduction of impurities in the scrap metal as follows: iron, 1500 ppm to 31 ppm; aluminum, 900 ppm to 41 ppm; nickel, 200 ppm to less than 52 ppm. Cost information developed by the committee from this work is presented in Tables 4-6 through 4-8.

In their conclusions, the Rocky Flats personnel stated they believed that operation of two full-scale cells would reduce substantially the cost of producing beryllium flake below the \$489 per pound value projected from their studies. The half-scale demonstration cell is available to support special-order work. However, before any further efforts are undertaken, the equipment should be modified to address health, safety, and environmental concerns. The equipment should then be able to produce 1000 to 1200 pounds of purified beryllium flake per year, since there currently is no primary source of high-purity beryllium in the western world. Small inventories exist that are being used for the fabrication of special-application end-product forms of beryllium.

### COST CONSIDERATIONS

Neither time nor resources are available to the committee to prepare independent cost analyses of the various metal extraction processes. However, it is possible to use the output of previous studies to at least estimate the relative economic impact of alternatives and to gauge and compare alternative courses of action.

Figure 4-2 shows a block flow diagram of the BWI process and economics as presented in the Task I Report (Zuehlke, 1982). This diagram shows

TABLE 4-6 Summary of Overall Costs

Item	Amount
Beryllium flake cost per pound <sup>a</sup>	\$ 489
Beryllium electrorefining start-up cost <sup>b</sup>	76,943
Beryllium chloride synthesis per pound <sup>a</sup>	143
Equipment costs	861,000
Equipment installation	1,706,000

<sup>a</sup>Direct operating cost only.

<sup>b</sup>Raw materials, load bulk salts, fuse, transfer to electrolytic cell.

TABLE 4-7 Beryllium Flake Production Direct Operating Cost per Day<sup>a</sup>

Item	Amount
Manpower	\$2,400
Power @ \$0.0367/kWh	13
Health, safety, and environment	12
Analytical	80
Salt loss due to dragout	<u>429</u>
Total cost per day <sup>b</sup>	\$2,934 <sup>c</sup>
Total production:	6 lb flake
Cost per pound of beryllium flake	\$ 489 <sup>d</sup>

<sup>a</sup>Based on \$50 per hour.<sup>b</sup>Cost does not include equipment depreciation; equipment cost + installation = \$2,567,000.<sup>c</sup>Based on 24-hour-per-day operation.<sup>d</sup>This does not include the start-up cost of the cell, which happens once every 3 to 5 years.

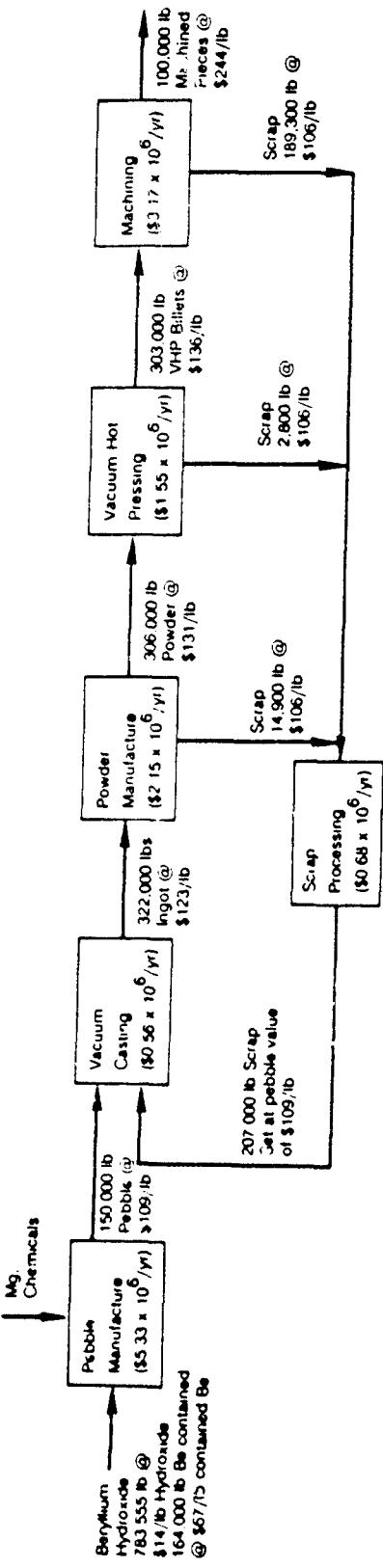
TABLE 4-8 Raw Materials Required to Start Up Electrolytic Cell

Item	Amount
Potassium chloride	\$ 440
Lithium chloride	4,800
Beryllium Chloride <sup>a,b</sup>	46,475
Beryllium scrap	N/C
Nitrogen	143
Sodium hydroxide	<u>50</u>
Total cost	\$51,908

<sup>a</sup>BeCl<sub>2</sub> used was Rocky Flats material at \$143 per pound.<sup>b</sup>Noah Chemical will provide BeCl<sub>2</sub> at the following prices:

\$275/lb in 100-lb lots

\$185/lb in 400-lb lots



1 Beryllium hydroxide costs are an estimate of its direct manufacturing cost (DMC)

2 Scrap to vacuum casting was set equal in value to pebble costs.

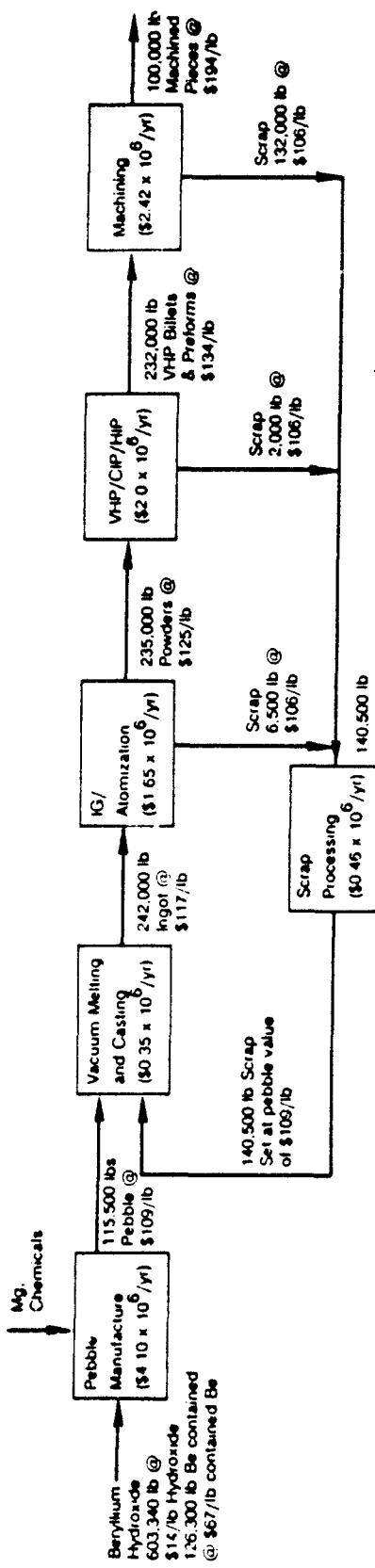
3 Figures in parentheses within blocks are annual operating costs.

4 \$/lb figures represent DMC costs of Beryllium at different stages of the process.

5 Overhead, depreciation, and profit are not included in these figures

SOURCE: Based on Task I DOE Report

FIGURE 4-2 Example of the current beryllium metal production cost structure (1982 constant dollars).



1 Beryllium hydride costs are an estimate of its direct manufacturing cost (DMC)

2 Scrap to vacuum melting and casting was set equal in value to pebble costs

3 Figures in parentheses within blocks are annual operating costs

4 \$/lb figures represent DMC costs of Beryllium at different stages of the process

5 Overhead, depreciation, and profit are not included in these figures

SOURCE: Based on Task I DOE Report

FIGURE 4-3 Estimated 1992 forecast beryllium production cost structure employing the gas atomization process (1982 constant dollars).

annual material flows between operating modules associated with 100,000 lb/year of shipped machined blanks and the associated annual operating costs, excluding overhead, depreciation, and profit for each operating module. If one assumes a transfer cash cost for beryllium hydroxide and sets scrap recycle values equal to pebble, then one can calculate the cash cost of beryllium through the process. Beryllium hydroxide at \$14/lb calculates to shipped beryllium machined blanks at \$244/lb. With this starting point, it is then possible to ask "what if" questions and to estimate the percent changes in transfer price associated with these changes.

The second case, shown in Figure 4-3, attempts to evaluate the economic changes associated with producing 40 percent of the shipped machined blanks via CIP and HIP near-net-shape processing of gas-atomized powder as a forecast for 1992. In this case, the internal scrap recycling is reduced by about 30 percent (see Chapters 5 and 6). The shipped beryllium blanks calculate out as having a cash cost of \$194/lb (1982 basis) or a reduction of \$50/lb, about 20 percent less than the 1982 case.

One can pose a similar question and ask what a \$10/lb and a \$20/lb reduction in beryllium extraction costs would do for the overall economics in the 1982 or 1992 scenario. The effects are as follows:

Year	Base Case Machined Beryllium Cost, \$/lb	Machined Beryllium Cost With Savings on Extraction			
		\$10/lb	Savings	\$20/lb	Savings
1982	\$244	\$229	6%	\$214	12%
1992	\$194	\$182	6%	\$171	12%

These data make it obvious that BWI has made the correct choice to concentrate on new forming and powder technologies before looking further at metal extraction alternatives. The second conclusion drawn is that the gains obtained from alternative extraction technology are marginal, 6 percent being the more realistic, when it is realized that increased environmental hazards and a formidable development program are also associated with a new extraction technology.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

- Currently there is no alternate process for metal extraction ready for commercialization other than the magnesium reduction process, and the identified market offers little incentive to develop one.

- Much improvement is believed possible with the magnesium reduction process.
- Electrorefining of beryllium metal scrap has had sufficient development to be ready for commercial implementation. Demand for large quantities of such metal does not exist today. However, this technology should be maintained on a small scale to provide a source of pure beryllium metal in the western world. The production of make-up beryllium chloride from the metal for the electrolyte requires further facility development to prevent excessive emissions.
- Implementation of NNS processing to the level of 40 percent of shipped part or blank production can reduce shipped beryllium costs by an average of 20 percent (for all shipments). By comparison, new beryllium metal production processes will probably realize savings of about one-third of this, i.e., about 6 percent.
- Improvements in the magnesium reduction process, coupled with good operator education and training, can permit operation that meets environmental emission standards.

#### Recommendations

- Redesign the magnesium reduction furnaces as vacuum-tight reducing reactors under an inert atmosphere.
- Improve the reduction furnace instrumentation so as to control the process variables to obtain the best yield of beryllium pebbles.
- Develop and design new and better-engineered large-capacity reduction furnaces that incorporate automated charging and take-away arrangements to allow for remote operation in totally enclosed systems.
- Develop an improved pebble inspection and sorting system.
- Continue and expand the education and training of process personnel to enhance production efficiency and minimize or eliminate detrimental excursions of emission standards.

#### REFERENCES

Block, F. E., R. E. Mussler, and T. T. Campbell. 1968. Beryllium Preparation by Metallic Reduction of Beryllium Chloride Vapor. Advances in Extractive Metallurgy, Paper 23, pp. 551-571. The Institution of Mining and Metallurgy, London.

Blue, D. D., and D. H. Baker, Jr. 1958. Electrorefining of vanadium, chromium, zirconium, and hafnium. United Nations Peaceful Uses of Atomic Energy: Proceedings, Second International Conference, Geneva, Vol. 4, p. 319, United Nations, New York (September).

Braunstein, J., G. Mamantov, and G. P. Smith. 1971. Advances in Molten Salt Chemistry. New York: Plenum Press.

Campbell, T. T., R. E. Mussler, and F. E. Block. 1970. Metallothermic Reduction of Beryllium Oxide. Metallurgical Transactions 1:2881-2886.

Gurklis, J. A., R. O. Beach, and C. L. Faust. 1952. Electrodeposition of Beryllium, Thorium, and Zirconium From Fused-Salt Baths. Office of Technical Services, AEC Dept. BMI-781 (November 4).

Illig, K., M. Hosenfeld, and H. Fischer. 1932. Electrolytic production of beryllium. Pp. 52-86 in Beryllium, translated by Richard Rimbach and A. J. Michel. New York: The Chemical Catalog Co.

Kaczynski, D. J. 1986a. Advanced Magnesium Reduction of Beryllium. DOE Contract DE-AC04-82AL18071 (July).

Kaczynski, D. J. 1986b. Task V Final Report. DOE Contract DE-AC04-82AL18071, pp. A-5 through A-23 (July).

Kaczynski, D. J. 1986c. The Modified Hall Process. Final Report, DOE Contract DE-AC04-82AL18071 (July).

Kaczynski, D. J. 1986d. The Degussa Process. DOE Contract DE-AC04-82AL18071 (July).

Mitchell, D. L., R. G. Nieweg, J. A. Ledford, M. J. Richen, D. A. Burton, R. V. Harder, and L. E. Watson. 1987. Beryllium Electrorefining. Rockwell International, Rocky Flats Plant, Report No. PSD87-051 (November 16).

Mitsui, L. 1982. Aluminum Composite Carbon-Alumina Anode in Chloride Melts. Japanese Patent J5 7 120 683.

Nettle, J. R., D. H. Baker, Jr., and F. S. Wortman. 1957. Electro-refining Titanium Metal. Bureau of Mines, Department of Investigations 5315.

Pistole, C. O. 1983. Summary of Beryllium Electrorefining Technology Developed by KBI Division of Cabot Berylco Inc. Rockwell International, Rocky Flats Plant, Report No. 3566 (May 27).

---

Schow, R. B. 1983. Electrowinning of Beryllium Chloride to Produce Metallic Beryllium. Task II, DOE Contract No. DE-AC04-82AL18071 (March 25).

VAW. 1982. Composite Carbon-Alumina Anode in Chloride Melts. German Patent DS 2 805 374.

Walsh, K. A. 1983. Beryllium Fluoride Recycle Elimination From Magnesium Reduction Process. Task II, DOE Contract DE-AC04-82AL18071, Vol. I, Section 12, p. 3.

Withers, J. C., and G. V. Upperman. 1982. Electrolytic Cell for the Production of Aluminum, U.S. Patent 4,338,177 (July). Composite Anode for the Electrolytic Deposition of Aluminum, U.S. Patent 4,342,637 (August).

Wong, M. M. 1972. Electrowinning of Beryllium. U.S. Patent 3,666,444 (May).

Wong, M. M., F. R. Cattoir, and D. H. Baker, Jr. 1960. Electrorefining Beryllium: Preliminary Studies. Bureau of Mines, Department of Investigations 5581.

Wong, M. M., R. E. Campbell, and D. H. Baker, Jr. 1962. Electrorefining Beryllium: Studies of Operating Variables. Bureau of Mines, Department of Investigations 5959.

Wong, M. M., D. E. Couch, and D. A. O'Keefe. 1969. Electrowinning of Beryllium. *J. Metals* 21(1):43-45 (January).

Wong, M. M., and J. E. Klosterman. 1964. Electrorefining Beryllium: Operation of a Prototype Cell. Bureau of Mines, Department of Investigations 6489.

Zuehlke, J. R. 1982. Review of Current Operations. DOE Contract DE-AC04-82AL18071 (July).

Zuehlke, J. R. 1983. Research and Development Study for Optimization of Beryllium Production Operations, Task II Report: Recommendations for Subscale Demonstration Models. DOE Contract DE-AC04-82AL18071 (April).

## Chapter 5

# IMPROVED METALLURGICAL OPERATIONS

Minimizing particulate air contamination is one of the most important considerations in producing metallic beryllium. The present limit of 2  $\mu\text{g}$  per cubic meter per 8 hours is difficult to maintain and monitor consistently in the workplace. At present, a step in producing metallic beryllium is to vacuum-melt and cast the metals into ingots. Because the as-cast ingots are very coarse-grained, the product is generally undesirable for working into a final shape. To overcome the as-cast coarse-grain problem, the current process involves vacuum melting, ingot casting, and reduction to powder. The principal route today to produce beryllium metal with suitable microstructure properties is by a mechanically produced powder (attrited, impact-ground, or ball-milled). The powder is produced from a 450-lb cast ingot that is machined to chips and further processed to powder for subsequent reconsolidation. This powder, when consolidated by (a) hot isostatic pressing, (b) cold mechanical pressing followed by sintering or hot isostatic pressing, or (c) vacuum hot pressing, yields a product that is suitable for fabrication into parts. However, the gas atomization process, whereby the pellets and scrap are vacuum-melted and gas-atomized in one step in a closed system, gives advantages both from the environmental contamination aspect and the preparation cost aspect.

## INERT GAS ATOMIZATION

Brush Wellman Inc. has been investigating the use of vacuum melting and inert-gas atomizing of beryllium to determine the characteristics and suitability of such a powder. Work to date has been carried out in an experimental 5-lb unit. BWI's findings show that the powder produced is spherical and gives a packing density of some 65 percent--a desirable property, particularly for near-net-shape fabrication. Also, the powder particles are generally polycrystalline. An important characteristic of gas-atomized powder is that the grain size of the final product remains stable after a 1000°C heat treatment. As expected, hot isostatically pressed spherical powder compacts show isotropic properties, and x-ray pole figures indicate a random crystallographic structure. Mechanical properties are consistent with grain size and basically follow the Hall-Petch yield strength relationship. The studies on the product from the 5-lb unit were very encouraging, so the unit is being scaled up to 12 lb; the 12 lb of beryllium is equivalent to a 50-lb unit for producing steel

because of the difference in density between beryllium and steel.

The Phase II expansion plans of BWI include a 100-lb vacuum-melting inert-gas atomization unit; this is equivalent to a 400-lb steel system. BWI's plans for future major beryllium product lines provide for producing a spherical gas-atomized powder that will be used directly, or an atomized powder that has been impact-ground to use the oversize powder from the atomization process. Thus, the trend is to inert-gas-atomize a spherical powder when the process is shown to be metallurgically satisfactory.

### NEAR-NET-SHAPE PROCESSING

Currently, the three methods for making powder from machining chips are attriting to produce a flake powder, ball-milling to produce an angular powder, and impact-grinding to produce a blocky powder. Of these three powders, the impact-ground powder is most suitable for near-net-shape fabrication. Attrited and ball-milled powders have insufficient packing density or flow characteristics for optimum use in the NNS, hot isostatic pressing (HIP) process. Currently, impact-ground powder is being used to make near-net shapes. It is well established, however, that spherical gas-atomized powder has better flow and packing density characteristics that make it amenable to NNS fabrication and handling for the HIP process.

Near-net-shape beryllium parts are produced by using a welded mild steel container of a shape and size that takes into account the shrinkage accompanying increase from 65 percent density to 100 percent density after hot isostatic pressing. The current procedure is to fill the mild steel container with impact-ground beryllium powder, vacuum outgas the powder-filled container, and seal it by crimping and welding the outgassing tube after sufficient outgassing has been achieved. The vacuum outgassing usually takes days. To reduce outgassing time, a "dynamic outgassing" system is being introduced, whereby vacuum outgassing can be done in a matter of hours. This is accomplished prior to loading the powder into the HIP containers.

An important feature of NNS technology is that considerably better yields can be achieved on initial input weight of powder to final product weight. For example, in using a vacuum-hot-press method, an initial 140 lb of powder results in a shipped weight of about 30 lb of preformed shapes, which is subsequently machined down to 6 lb, as shown in Figure 5-1. Total material utilization obviously is quite poor. With the use of a shaped container and hot isostatic pressing to near-net shape, approximately 25 to 45 percent of the initial powder used in the vacuum hot pressing process is needed, depending on the exact shape of the final product. Thus, considerable savings in starting powder requirements would result if the NNS process were broadly adapted for making beryllium parts.

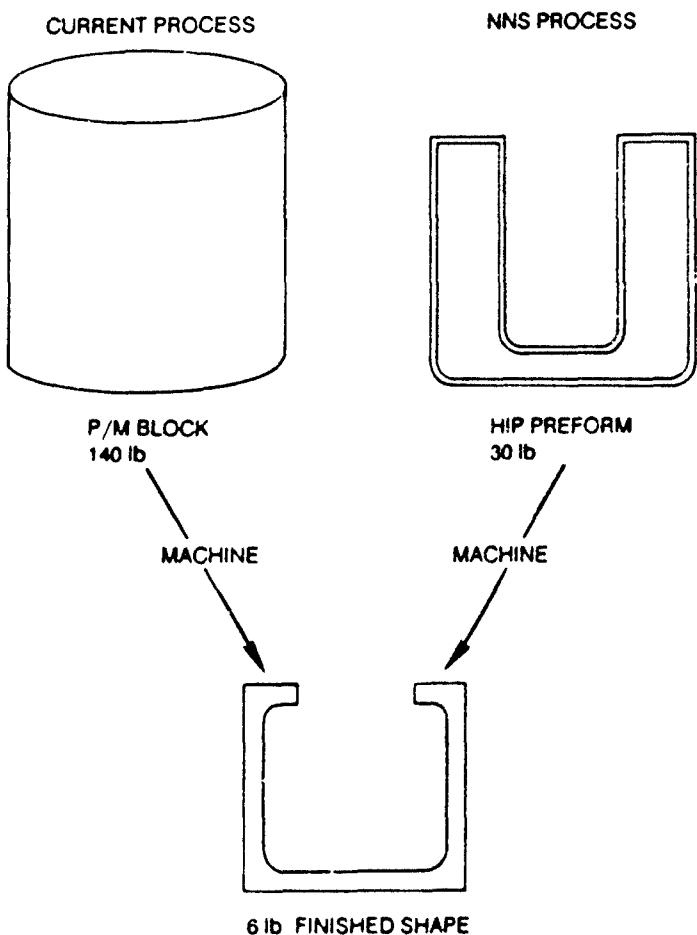


Figure 5-1 Schematic of material and machining savings by using HIP preform processing.

In addition to a major cost saving, the smaller amount of powder handled would help improve environmental problems that result from handling large volumes of powder. The process also offers an opportunity for adapting it to a closed system.

#### ENVIRONMENTAL AND COST CONSIDERATIONS

The main sources of air contamination today are found in processing steps from the vacuum-melted ingot to the final solid product. These include machining to produce chips from the vacuum-melted ingot, followed by converting it to a powder by attriting, impact-grinding, or ball-milling. The powder is then handled through the container-loading and compacting stages, followed by machining the compact to a final shape. These

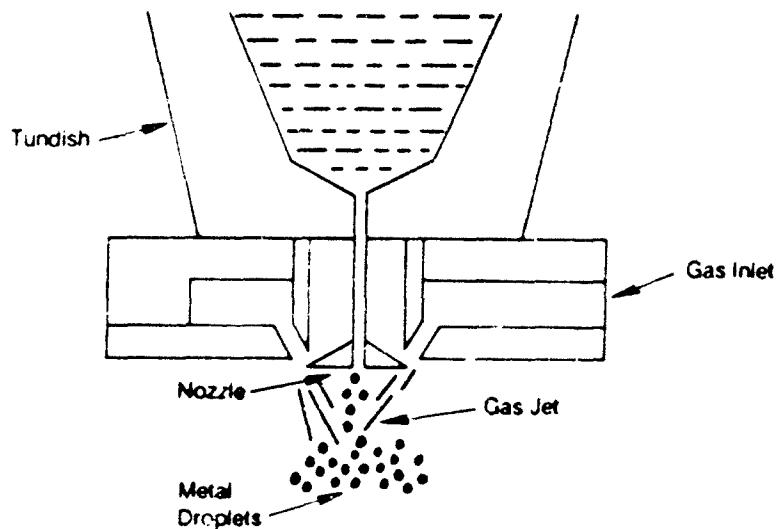
operations basically are carried out dry, so the chance for fine dust particles to escape is reasonably high compared to the earlier wet steps in the processing.

Employing the vacuum-melting inert-gas-atomizing process, the entire process can be carried out in a closed system. A gas atomizing system currently used in the production of superalloy powder (Figure 5-2) is similar to a system applicable to beryllium. In such a system, the melting charge is loaded into the vacuum-melting crucible followed by sealing the system, and the system remains sealed throughout the melting and the inert-gas atomizing to produce the powder. The atomized powder is then collected in an evacuated or inert-gas-filled container that is coupled through a valve to the cyclone or the base of the atomizer chamber where the powder collects. The sealed powder-filled container is then transported to an inert-gas-filled glove box system. The container is positioned above the glove box, which permits the powder to be gravity-fed into the inert-gas-filled glove box to load a shaped metal HIP container. The container is then outgassed and sealed prior to HIP consolidation.

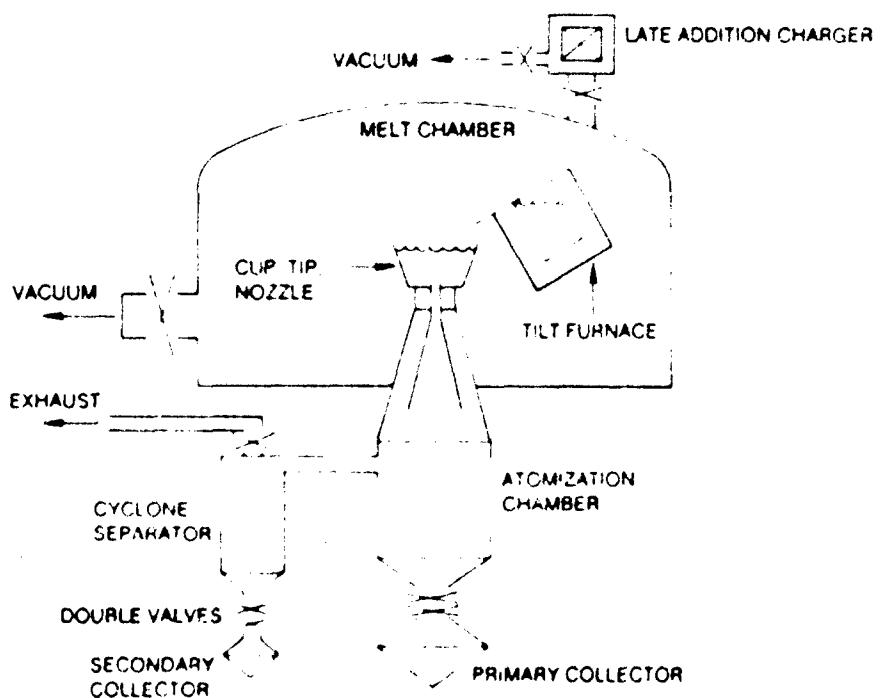
The entire handling involves no exposure of the powder to the atmosphere at any stage, thereby reducing significantly the potential for environmental contamination. By employing a spherical powder produced by the inert-gas-atomization process, followed by NNS fabrication to approximately final form, cost savings of 30 to 40 percent are estimated (see Chapter 4). The yields from vacuum melting to powder may, after an appropriate development program, be as much as 90 to 95 percent, and the yields from powder preparation to the NNS fabrication would vary, depending on the complexity and size of the part being produced. In addition, the final yield should be substantially higher than that obtained from the current process, in which the solid piece is machined to the final part configuration. Substantially less machining is required with the near-net-shape process, as compared with the conventional solid compact machine-to-shape work. By generating considerably less machining chips, the result is less environmental contamination and less beryllium scrap. A comparison of the steps in the existing process and of the gas atomization process (Figure 5-3) shows that significantly fewer handling steps are involved in the latter process.

## SUMMARY

On the basis of the environmental control and cost aspects of the new approach to making beryllium metal by vacuum melting and inert-gas atomizing followed by NNS fabrication, the shift from conventional or currently used methods for making beryllium parts is considered essential for overcoming some of the major problems of beryllium metal processing. The technology for gas atomization and near-net-shape fabrication is well



A Typical atomization nozzle



B Typical overall metal atomization system

**Figure 5-2 Gas initial atomization system schematic for superalloy powder production.**

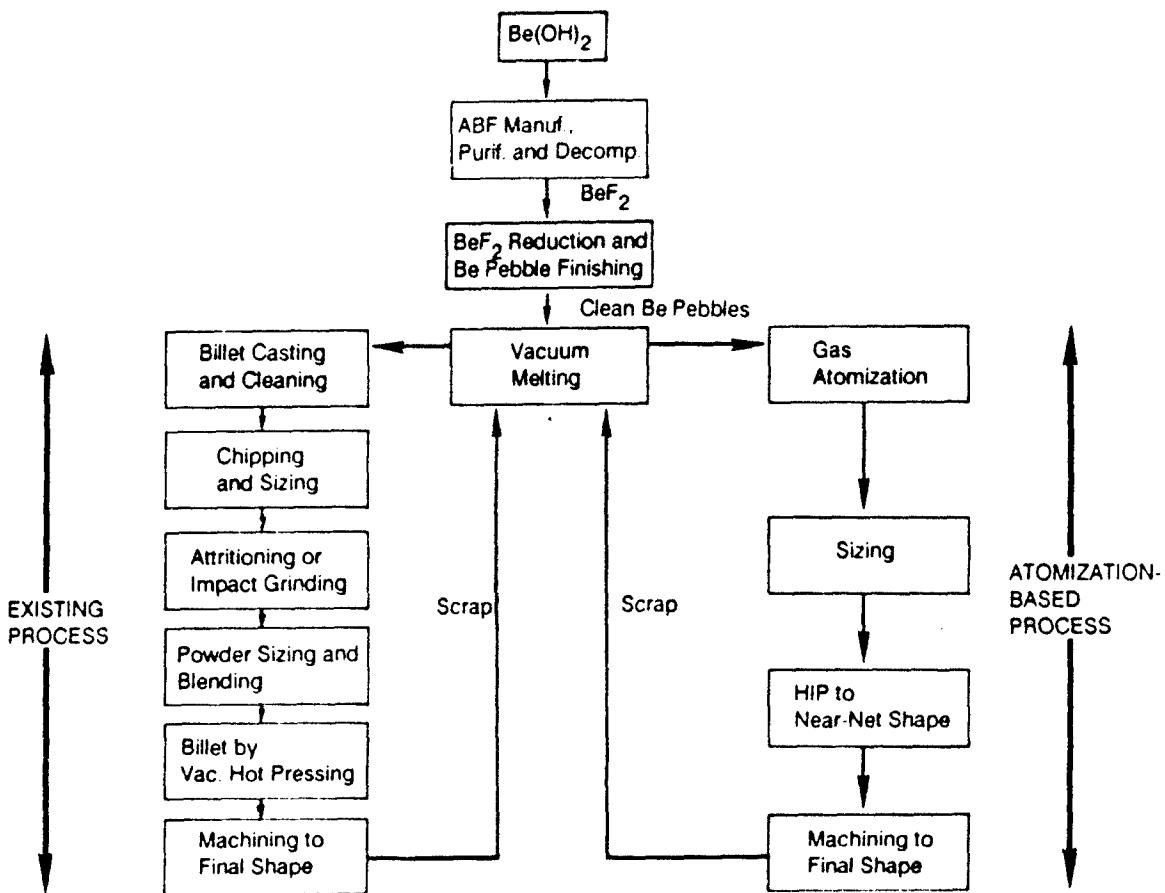


Figure 5-3 Comparison of existing process with the atomization-based process.

established for other metal systems such as superalloys and high-alloy steel. The status of this field was comprehensively reviewed in two National Materials Advisory Board reports (1981; 1982) as well as elsewhere (Anderson and Kemppainen, 1986; Anderson and Figliola, 1988; Moll, 1986; Rizzo et al., 1982; Chandhok et al., 1985). These publications show that the state of the art developed for other metal systems is a commercial one and that the systems technology required for making atomized beryllium powder is well in place. Further advances and newer facilities have been introduced since these studies. Nevertheless, the information presented there shows clearly that many metal atomizers and HIP facilities are available in the United States. These facilities may not be available for the preparation and consolidation of beryllium powder, primarily because of fear of contamination associated with leaky storage and NNS containers. The processes of vacuum melting, inert-gas atomization, and NNS processing

have been used commercially for many years. Thus, the basic process technology involved in preparing beryllium metal near-net shapes is well established, so success is virtually assured.

Further experimentation would be required to develop information specific to metallic beryllium component production. An R&D program is needed to determine the optimum operating parameters for making suitable gas-atomized beryllium powder and NNS beryllium parts. Inasmuch as a great deal of the basic technology is already known, the recommended R&D program could be completed within 6 to 12 months. In addition, procedures to minimize air contamination need to be investigated and incorporated into the new production process.

Because of the importance of a continuous supply of beryllium metal for DOD and DOE applications, strong consideration should be given to having more than one vacuum-melting, gas-atomizing, and HIP facility for making beryllium metal near-net shapes. For example, such a system located at the Rocky Flats Plant, where DOE scrap could be used as well as virgin charges of beryllium, would provide added assurance of a continuous supply of the product. Also, the technical information generated would supplement that developed by BWI during production and experimentation on the new units. The cost of such a system would be relatively moderate, considering the importance of maintaining a continuous supply of this important metal.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

- The process of gas atomization and near-net-shape fabrication should substantially reduce environmental contamination and production costs.
- The basic technology is already in place for metal gas atomization and near-net-shape fabrication, based on established commercial powder metallurgy superalloy production methods.

### Recommendations

- Initiate a moderate R&D program to optimize metal gas atomization and near-net-shape practices for beryllium.
- Establish a second gas atomization and near-net-shape facility to ensure a continuing supply of beryllium powder and a fabrication capability.

**REFERENCES**

Anderson, I. E., and M. P. Kemppainen. 1986. Undercooling effects in gas atomized powders. Proc. of 1986 Hume-Rothery Memorial Symposium, AIME-TMS 115th Annual Meeting, March 2-6.

Anderson, I. E., and R. S. Figliola. 1988. Observations of gas atomization process dynamics. Modern Developments in Powder Metallurgy, Vol. 18.

Chandhok, V. K., J. H. Moll, C. F. Yolton, and G. R. McIndoe. 1985. Advances in P/M Titanium Shape Technology Using the Ceramic Mold Process: Overcoming Material Boundaries. Proc. of 17th Nat. SAMPE Tech. Conference, pp. 495-506.

Moll, J. H. 1986. Production and characterization of rapidly solidified steel, superalloy and titanium alloy powders made by gas atomization. Progress in Powder Metallurgy, Vol. 42, MPIF, p. 721-740.

National Materials Advisory Board. 1981. Superalloys From Powder: Production and Properties. NMAB Report No. 369. Washington, D.C.: National Academy Press [limited-distribution document available from Defense Technical Information Center].

National Materials Advisory Board. 1982. Rapid Solidification Processing: Status and Facilities. NMAB Report No. 401. Washington, D.C.: National Academy Press [limited-distribution document available from Defense Technical Information Center].

Rizzo, F. J., J. Lane, and J. H. Moll. 1982. Production of P/M Near-Net Shape Superalloys Hardware. SAE Technical Paper 821515.

## Chapter 6

# SCRAP RECYCLING

Sources of recycled solid beryllium material can be classified as internal or external to the manufacturing process. In addition, the form of the recycled beryllium--e.g., solids, chips, and baghouse cleanings--and the degree of contamination provide further dimensions of variability. To add to the complexity, the growing importance of near-net-shape processing and the forthcoming production of beryllium powder via melt to gas-atomization processing promise to alter dramatically the future ratio of recycled scrap to finished part manufacture.

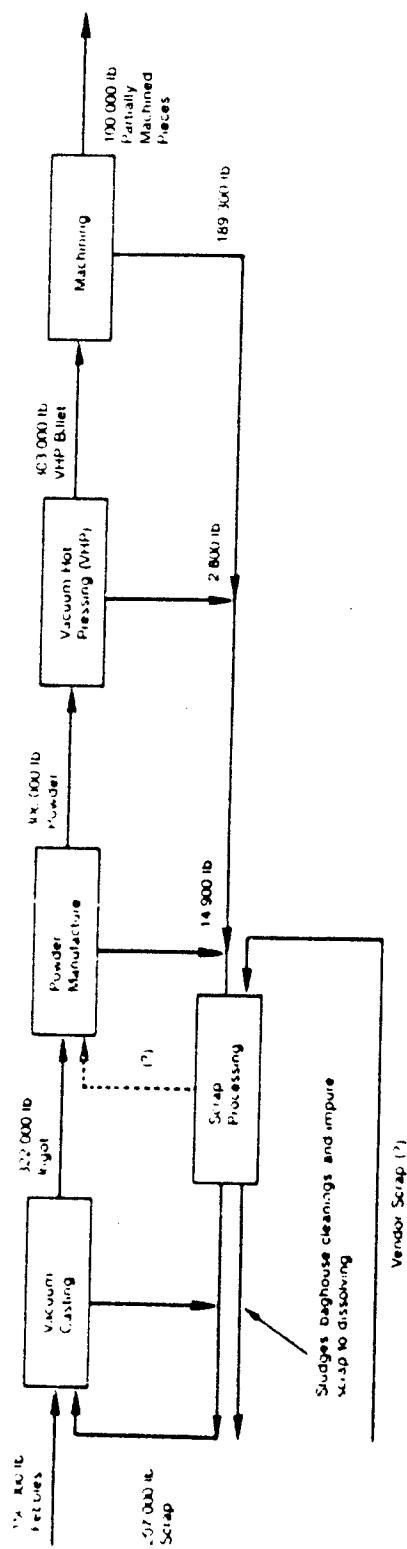
### CURRENT STATUS

A picture of the relative flows of beryllium scrap versus pebble can be gleaned from the 1982 U.S. DOE Task I Report (Zuehlke, 1982), as shown in Figure 6-1.

Brush Wellman Inc. does not normally purchase vendor scrap. For special situations, however, such as periods of need for increased capacity associated with large National Defense Stockpile purchases, BWI will bid competitively on the open market for vendor scrap.

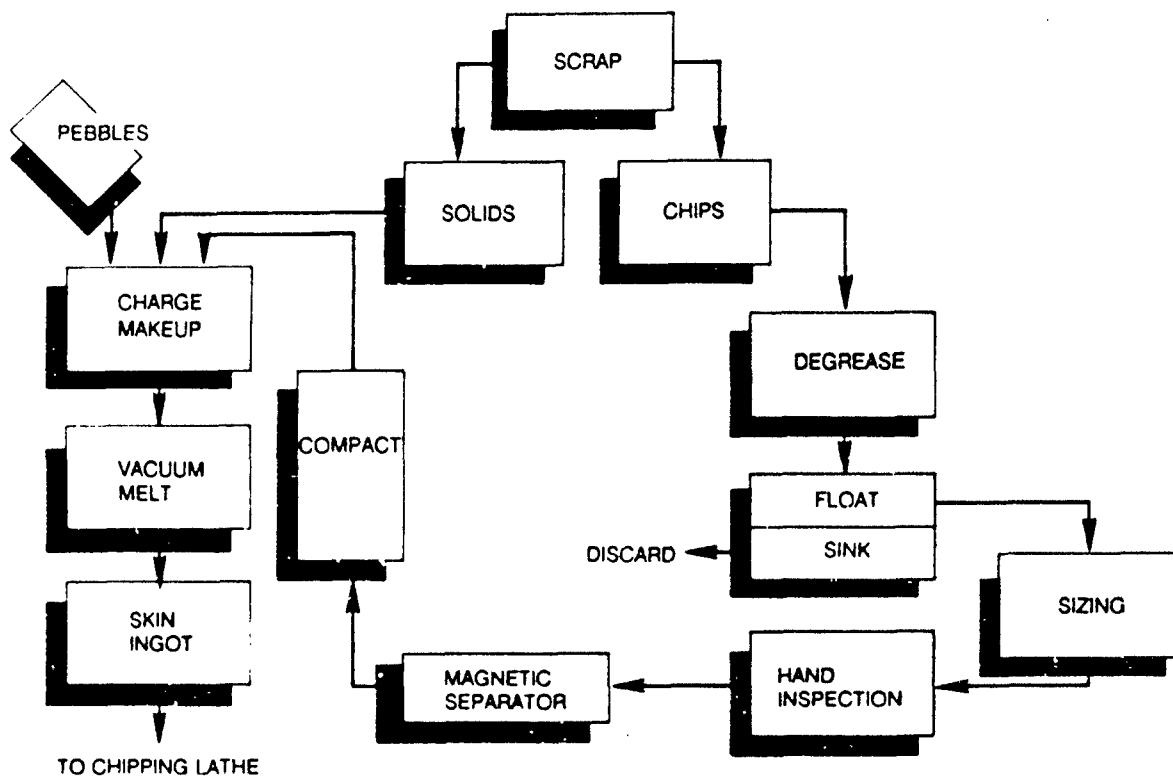
The BWI scrap-processing operation is shown in Figure 6-2. Input materials, characterized as solids and chips, are normally in the weight ratio of 1:7 respectively; sludges, baghouse cleanings, etc., are not shown. Solid materials are sized, weighed, inspected, and analyzed before going to the vacuum melter. Chips are normally degreased, separated via a sink-float method (depending on source), magnetically screened for iron removal, visually inspected, x-rayed, chemically analyzed, and stored with assigned lot numbers. When released by quality assurance personnel, chips are compacted into 2-in.-diameter by 1- to 2-in.-thick pucks of about 70 percent density for recycling by vacuum melting. The pucks are used because they are more responsive to induction melting, since they melt faster than loose chips.

It should be noted that the partially machined pieces supplied by BWI to the DOD and DOE are further machined and usually result in a scrap-to-finished-part ratio of about 3:1 (Cynthia Gonsalves, presentation to the committee, January 20, 1988). At a shipping level of 100,000 lb annually of partially machined pieces by BWI, vendor-generated scrap should amount to



**Figure 6-1 1982 beryllium material flow (figures do not add because of rounding of estimates).**

(7) indicates alternative actions not practiced for producing all shapes.



**Figure 6-2 Scrap recycling process flow. (Source: Producing Defect-Free Beryllium and Beryllium Oxide, Brush Wellman Engineered Materials, May 1985).**

75,000 lb annually. Not all of this is of high enough purity for recycling to powder manufacture or vacuum casting. The 75,000-lb figure seems incredibly high, but DOE, whose beryllium purchases are far less than DOD's, itself generates 6,000 lb annually of scrap and machine chips. The amount or disposition of the annual DOD beryllium scrap was unavailable to the committee. DOD does not purchase beryllium stock directly from BWI, and the DOD machining subcontractors sell the resulting scrap on the open market. The material probably ultimately ends up in alloys. This lack of control of beryllium stock and scrap by DOD requires further analysis.

The Rocky Flats plant (the prime DOE facility contractor is Rockwell International) has been inventorying its in-house scrap and is seeking a recommendation as to its disposition. The current Rocky Flats scrap inventory is as follows (R. Jiaocetti, private communication, April 20, 1988):

---

Solid and ingot scrap	33,000 lb
Dry machine chips	<u>24,000</u> lb
Subtotal	57,000 lb

Over the next 5 years the following amounts of scrap are expected to be generated:

Solid and ingot scrap	1000 lb/year
Dry machine chips	<u>5000</u> lb/year
Subtotal	6000 lb/year

At open-market scrap prices, currently about \$50 to \$70 per lb, the anticipated scrap inventory in 1993 of 87,000 lb (57,000 lb + 30,000 lb) will have a value of \$4 to \$6 million.

## TRENDS

Increased use of NNS powder processing and the use of gas atomization for powder production promises to reduce in the future the amount of recycled scrap available, relative to finished parts. NNS is not expected to totally replace vacuum hot pressing and machining, since both the shape of the finished piece and the number of units to be made will affect the choice of processing that is employed. BWI staff has projected that NNS parts will amount to about half of BWI's beryllium metal sales dollars; this in turn may mean about 40 percent of the shipped poundage. The impact of scrap recycling changes is compared in Table 6-1. The amount of internally and externally generated scrap is forecast to drop about 30 percent by 1992 at the same time that a constant supply of finished parts is maintained. Greater use of NNS will further reduce the need for scrap recycling.

## Study by Rockwell International, Rocky Flats Facility

A study funded by DOE evaluated a separate scrap recycling facility at Rocky Flats (Rockwell International, 1988). The key features of this evaluation included the following:

- Annual capacity of 20,000 lb/year of NNS blanks produced via atomized powder and HIP.
- Purification of 25 percent of the scrap via electrorefining.
- Maintenance of airborne beryllium concentration levels below 1  $\mu\text{g}$  per cubic meter.

TABLE 6-1 Comparison of Scrap Recycling Trends

Year	Processing Technique	Relative Material Flows		
		Powder	Delivered Form	Finished Part
1982	Impact grinding and attrition, VHP, machining, final machining	12.3	4.0	1.0
		Internal scrap 8.3	External scrap 3.0	
1992	60% impact grinding, VHP, machining, final machining	7.4	2.4	0.6
1992	40% melt atomization, NNS, machining, final machining	1.6	0.8	0.4
		9.0	3.2	1.0
Total		Internal scrap 5.8	External scrap 2.2	

The Rocky Flats estimated capital investment requirement of \$242 million for implementing this capability is high and reflects the stringent design conditions set for the plant, possibly based on radioactive material processing. To illustrate this point, compare Rockwell International's investment figure of \$12,100 per annual pound against the following: BWI's total property, plant, and equipment (as stated in BWI's 1986 annual report) comes to \$230 million, not counting depreciation. If capital is apportioned to sales, then the whole metal operation (hydroxide to blanks, which accounts for about 15 percent of sales) accounts for a \$35 million investment ( $0.15 \times \$230$  million). At present-day replacement costs, the figure comes to about 3 times this, or \$105 million. At 100,000 lb of blank production capacity, this comes to about \$1000 per pound, which includes pebble manufacture starting from the hydroxide. It should be recognized that the BWI plant is not designed to maintain airborne beryllium concentrations below 1  $\mu\text{g}$  per cubic meter, as was the Rockwell design.

In summary, the Rocky Flats estimate runs much higher than expected.

A primary contributor to the extraordinarily high capital requirement is the fact that some of the design criteria apparently are those employed for handling plutonium and are difficult to justify for beryllium processing.

### Electrorefining

Although the cost numbers, particularly the capital, presented in the Rockwell International study are high, the concept of scrap recycling with electrorefining should not be dismissed. The cost figures for electrorefining presented by Rocky Flats personnel (Mitchell et al., 1987) and summarized in Chapter 4 are dominated by labor costs. It is reasonable to assume that, with the development of an acceptable synthesis facility for make-up electrolyte beryllium chloride and scale-up of the electrolytic cells, the electrolytic beryllium flake cost of \$489/lb, with no charge for beryllium scrap, could possibly fall to \$150/lb. The electrolytic flake could then be combined with beryllium scrap to produce a feed to the vacuum melting furnace valued at \$100 to \$125/lb, assuming scrap valued at \$50 to \$70/lb (Figure 6-3). These costs are quite competitive with those of the BWI feed material to the vacuum melting.

The decision as to whether the electrorefining and processing of the upgraded scrap should be done at a government facility, at BWI, or at an independent contractor is not addressed here. Control of DOE and DOD scrap, combined with reprocessing, including electrorefining, has the potential to reduce outside purchase requirements or pebble manufacture by about 50 percent. This reduction would be consistent with the stated objective of ensuring a continued supply of beryllium metal.

### Recycling at Royal Ordnance Factory, Cardiff

A less sophisticated and less expensive approach to internal scrap recycling is practiced by the Royal Ordnance Factory at Cardiff, U.K.

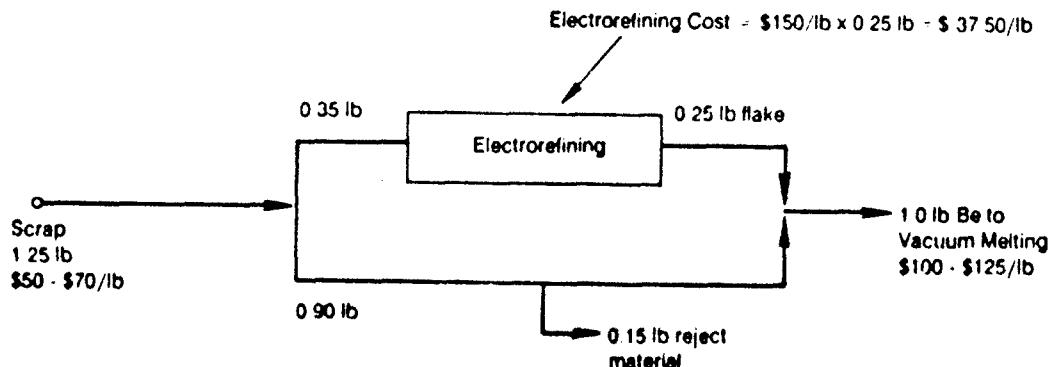


Figure 6-3 Scrap recycling by electrorefining furnace, as shown in Figures 4-1 and 4-2 (Chapter 4).

(Dawson, 1986). The facility produces about 1000 kg/year of recycled powder and has a capability to produce up to 4000 kg/year. It employs small vacuum-casting units, swarf cutters, impact mills, and various presses but does not practice chemical purification of recycled scrap. Apparently by blending recycled materials with purchased beryllium from BWI, the plant is able to meet product purity specifications.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

- The introduction of NNS processing should reduce internal and external scrap generation by approximately 30 percent.
- The DOD should control the beryllium machining scrap generated by its subcontractors as well as other scrap. The DOE currently does control its beryllium scrap.
- The Rockwell International study for a scrap recycling facility, including electrorefining and incorporating some plutonium handling design criteria, resulted in a unit capital charge much higher than BWI's currently estimated unit-replacement capital.
- Electrorefining costs can be reduced to a level where a recycling stream composed of 75 percent scrap and 25 percent electrorefined flake can give a cost comparable with BWI-produced pebble.
- Control of DOE and DOD scrap, plus electrorefining, could provide a feed quantity amounting to about 50 percent of the BWI pebble capacity.
- There appears to be merit in establishing a facility for scrap recycling that would incorporate electrorefining, gas atomization, and NNS processing.

### Recommendations

- Introduce NNS processing in the production scheme as an effective way to reduce internal and external scrap generation.
- Initiate a DOD beryllium scrap control program, similar to that used by DOE, for the recovery and recycling of scrap from machining subcontractors and other sources of scrap.
- Examine the merits of using the electrorefining process in a scrap recycling stream that uses both scrap and electrorefined flake.

- Consider having a separate scrap recycling facility that would include electrorefining, gas atomization, and NNS processing capabilities.

#### REFERENCES

Dawson, I. A. 1986. UK/USA Beryllium Information Exchange. Avis 166, Beryllium Metals Production and Recycling Facilities, Royal Ordnance Factory, Cardiff (U.K.).

Mitchell, D. L., R. G. Nieweg, J. A. Ledford, M. J. Richen, D. A. Burton, R. V. Harder, and L. E. Watson. 1987. Beryllium Electrorefining. Rockwell International, Rocky Flats Plant Report PSD87-051 (Nov. 16).

Rockwell International. 1988. Scope and Estimate: Beryllium Scrap Recycle Facility. Rocky Flats Plant Special Report (Mar. 16).

Zuehlke, J. R. 1982. Task I Report: Review of Current Operations. U.S. DOE Contract DE-AC04-82AL18071.

## Chapter 7

# WORKPLACE HEALTH CONSIDERATIONS AND MONITORING

This chapter reviews data on the health effects from exposure to beryllium particulates and efforts in environmental monitoring of beryllium levels in the workplace. Data on process shortcomings and recommended changes are covered in Chapter 3 and are not repeated here.

## HEALTH CONSIDERATIONS

The two medical conditions that are of greatest concern in a beryllium metals production facility are chronic berylliosis and lung cancer. As result, the issue is whether the current atmospheric standard of  $2 \mu\text{g}/\text{m}^3$  for in-plant exposure, which has not been met consistently in U.S. facilities, is adequate as a suitable target for improved engineering controls to protect the health of workers. No discussion of the evolution of this standard will be given here, but a review of the history and current state of knowledge about beryllium diseases is found in a recent publication by Kriebel and associates (1988).

### Chronic Berylliosis

Chronic berylliosis is a chronic inflammatory disease of the lung that has an immunological basis; it is a thickening and scarring of the walls of the air sacs (alveoli) of the lung<sup>1</sup>. The induction of immune response to beryllium in the lung leads to a chronic inflammatory process in lung walls, which impedes oxygen transport and stiffens the lung. The effects may progress from subclinical diminution of lung function, which may be evident only on exercise, to shortness of breath at rest, and finally to heart failure and death. Important factors are that the dose response is not known and that there is an inherent immunological responsiveness to beryllium. If immunological responsiveness is absent, the individual does not get chronic berylliosis.

---

<sup>1</sup>The evidence is strongest that chronic berylliosis is caused by insoluble beryllium particles, most commonly by BeO or beryllium metal where the latter is coated with BeO.

Ever since the landmark paper of Sterner and Eisenbud (1951), chronic berylliosis has been recognized as having an immunological basis, where only a small proportion of the exposed population has the immunological potential to develop overt disease. By implication, if the immunological potential of susceptible individuals could somehow be recognized early on, the chronic berylliosis problem would be averted by preventing exposure in such individuals. The basis for the  $0.01 \mu\text{g}/\text{m}^3$  out-of-plant standard was the observation that no out-of-plant cases occurred at lower estimated exposure levels. The rationale for the  $2 \mu\text{g}/\text{m}^3$  in-plant standard is less well defined but basically amounts to the judgment that the standard is as low as can be practically achieved.

Chronic berylliosis cases are still occurring. In the BWI plant at Elmore, 13 cases of overt chronic berylliosis have occurred; 11 of these began exposure 20 to 30 years ago, and the other 2 cases began exposure 3 to 7 years ago and were diagnosed in the past year or two.

A recent study of the beryllium machinists at the Rocky Flats plant has been informative (Kreiss et al., 1988; Newman et al., 1989). Of 58 currently exposed individuals, 51 were given a lymphocyte transformation test on their peripheral blood; this is a test that measures immunological sensitization of the exposed individual to beryllium. Of the 51 workers, 6 had positive results. Five of the six individuals agreed to a more detailed examination that included lung biopsy for the presence of beryllium granuloma. Four of the five individuals showed a strongly positive lymphocyte transformation test for lymphocytes washed out of the lung and had definite evidence of chronic berylliosis by biopsy. None of the five individuals had come to attention previously in prior screening efforts during physical examination, lung function tests, and chest x-ray. All of the five had some minimal symptoms, and most had normal pulmonary functions and no chest x-ray abnormalities. All of the positive cases were in the 20 machinists that were first exposed at least 10 years ago. This study indicates that the older employees have a 20 percent prevalence of chronic beryllium disease. However, it is reported that lymphocyte transformation tests, based on peripheral blood, have only half the detection efficiency as the same test done on lymphocytes washed out of the lung (Rossman et al., 1988). Hence, the prevalence of chronic beryllium sensitivity in the older workers may be greater than 20 percent and could be as high as 40 percent. These results suggest that some degree of immunological responsiveness to beryllium exposure is common in the general population. However, the results of past studies have indicated that the incidence of chronic beryllium disease is only between 3 and 6 percent in individuals exposed above today's standard.

If, as it seems, a substantial proportion of the population is susceptible to the development of some degree of chronic berylliosis, the question arises as to the objective of the exposure standard for beryllium: Is

it only to protect against responses so severe as to be readily diagnosable by pulmonary function and x-ray abnormalities? Or is the standard supposed to protect individuals to a level where the granulomatous response is so minimal as to have negligible effects on pulmonary function even under stress? Obviously, the latter case would be ideal. Not enough is known about the pathodynamics of chronic berylliosis to construct a model that reliably predicts the air concentration that would not produce more than an acceptable amount of granulomatosis. It is only possible to predict the magnitude of alveolar deposition given the concentration and size distribution of inhaled particles.

A number of questions arise on the immunological response of a susceptible individual. The absence of information regarding dose-response for sensitization and for inflammatory effects means that there is no reliable basis for predicting the consequences of low-level exposure to beryllium. Furthermore, there is the possibility that chronic berylliosis is basically a nonthreshold process. All in all, these considerations argue that, among those individuals who are sensitive to beryllium, there is no assurance of a threshold for the induction of chronic berylliosis, and hence worker exposure should be minimized to the greatest extent feasible.

#### Lung Cancer

The evidence for the carcinogenicity of beryllium has been summarized recently by EPA's Carcinogen Assessment Group (U.S. Environmental Protection Agency, 1987). The National Institute of Occupational Safety and Health is currently examining this effect in the beryllium industry. Lung cancer has been induced in two animal species, rats and monkeys, either by the inhalation or instillation of particles of beryllium sulfate, phosphate, oxide, and beryl ore. There is some evidence that beryllium is mutagenic and can damage the genetic characteristics of cells. Several studies on beryllium workers have shown some increase in lung cancer, but enough uncertainties exist in the data to make the evidence equivocal.

The Carcinogen Assessment Group rated beryllium in all its forms as a probable human carcinogen. The lung cancer risk, calculated from the animal data for a continuous lifetime exposure to 1  $\mu\text{g}/\text{m}^3$ , is 0.2 percent. The risk estimate from the equivocal human lung cancer data is the same. This risk number, based on animal data, is a crude upper-limit estimate of the incremental excess risk based on the use of a linear nonthreshold dose response model. It is upper-limit in the sense that the true risk is not likely to be greater but could be considerably lower. An occupational exposure pattern (40 years, 50 weeks/year, 40 hours/week) at the current standard of 2  $\mu\text{g}/\text{m}^3$  would have an associated lung cancer risk of  $5 \times 10^{-4}$ . This means that there could be 5 extra lung cancer cases in a work force of 10,000 people who were occupationally exposed for 40 years. It should be

noted that such a population would be expected to have about 300 cases of lung cancer without any beryllium exposure. This value is low compared to the risk associated with the occupational standards for some other carcinogens.

## BERYLLIUM MONITORING RESULTS

The techniques for monitoring the workplace for beryllium particulates have been in place for years. This section reviews data from various facilities and identifies specific needs in monitoring beryllium levels and collecting data that could help to more effectively ensure worker safety.

### **Brush Wellman Inc., Elmore, Ohio**

The in-plant environmental monitoring program of the Elmore plant follows the sampling procedures established by the Atomic Energy Commission during the 1950s (NIOSH, 1972). The method utilizes high-volume samplers, drawing air at approximately 250 liters/minute through 10.5-cm-diameter (No. 4 Whatman) filter papers. Approximately 350 total dust samples are collected monthly by various means for the evaluation of 19 beryllium processing operations. From limited data obtained from side-by-side personal samplers (NIOSH, 1976), it would appear that from one-third to two-thirds of the mass concentrations of collected aerosols is respirable (less than 10  $\mu\text{m}$  in diameter). The majority of the samples collected are area samples, taken in the region of worker activity at a particular operation. These are usually 30 minutes to 1 hour in duration; samples of 8 hours' duration are collected at selected locations of special concern. For these latter samples, a 14-liter/minute pump draws air through a 25-mm-diameter (No. 4 Whatman) filter paper. Breathing-zone samples evaluate specific short-term activities that may be done by a worker in a particular operation. These samples are of 2 to 10 minutes duration, depending on the process being monitored.

Daily weighted average (DWA) concentrations are calculated using the measured concentrations and a time and motion analysis of various worker activities in a particular plant process. The area and breathing zone samples are weighted according to the time and number of workers expected to encounter those concentrations at a particular operation during the course of a normal working day. Two DWAs are calculated. In one, the "potential" DWA, the measured concentrations are utilized as described. In the second, the "actual" DWA, are work activities that require the use of a respirator and are rated as having zero exposure. This last procedure is deemed inappropriate because most respirators used are of the half-face variety. These respirators are rated to provide a protection factor of 10, but improper fit and less than continuous use by a worker would reduce the potential protection. Thus, for greater accuracy, a percentage of the

"potential" exposure, perhaps 20 percent, should be used to estimate "actual" exposure when respiratory protection is required. However, the jobs requiring respiratory protection are relatively few, and thus overall actual DWAs would be affected only to a small degree. Also included in the DWA calculations are exposures encountered in nonwork locations, such as change rooms and the cafeteria. These concentrations do relate to a worker's DWA but do not apply to the exposure at the process being monitored.

It should be noted that most DWA estimates at BWI establish average concentrations for particular processes, rather than for individual workers. They may not be applicable to individual workers employed at a particular plant operation unless the worker performs all the operation tasks as time-weighted in the sampling program, or unless the sampling for a process represents only the activities of the full-time process operator. Similarly, they are not directly applicable to workers, such as supervisors, whose job may take them through several operations. Maintenance employees, in particular, appear to fall outside the scope of these DWA estimates. Furthermore, the BWI sampling program neither makes use of personal lapel samplers to evaluate individual exposures nor utilizes swipe samples to monitor surface contamination.

Data have been supplied to the committee showing the quarterly DWAs for 19 plant operations for the years 1971-1986 (Kaczynski, 1986). Potential DWAs were shown from 1978. The sampling program at BWI does not focus on or neglects exposures that exist during upset conditions. Company personnel believe that excess releases during upset conditions are sampled to the extent they happen to occur. Thus, the data presented in the Task V Final Report (Kaczynski, 1986) are considered to reflect average process concentrations during all conditions of operation (P. R. Wilson, personal communication, July 1988). Since 1981, a concerted effort has been made to reduce concentrations to achieve compliance with the  $2 \mu\text{g}/\text{m}^3$  standard of the Occupational Safety and Health Administration (OSHA). The effects of this effort were particularly noticeable in the years 1986 and 1987. Prior to 1982, only 3 of the 19 plant processes maintained air concentrations below the standard; however, by 1986, eight additional processes were brought into general compliance with the standard. Additional improvements installed during 1986 and 1987 brought most remaining processes into compliance. During 1987 only 2 of 73 quarterly actual DWAs and 3 of 73 quarterly potential DWAs exceeded  $2 \mu\text{g}/\text{m}^3$ .

It should be noted that these concentration averages are only indicative of workplace concentrations and the trends with time. They do not represent time-weighted averages for the plant work force, nor do the individual measurements, consisting of averages, represent the range of individual time-weighted average daily exposures. Furthermore, the possibility exists that systematic errors occurred in the concentration measure-

ments because of fluctuations in the line voltage to the sampling pumps (see section on New York University experiments later in this chapter). The degree to which this has occurred cannot be assessed. However, such fluctuations could lead to underestimates of concentrations by as much as 30 percent.

Limited data on earlier Elmore plant concentrations are provided in the beryllium criteria document (NIOSH, 1972). Tables for "Plant B" in that document give data on air concentrations in the Elmore facility (P. R. Wilson, personal communication, August 1988). Table 7-1 lists the distribution of breathing zone and general area samples reported for a variety of operations in the plant. Because different operations were sampled during different years, direct year-to-year comparisons cannot be made. Nevertheless, the overall data would be representative of conditions at Elmore during the late 1950s and early 1960s. Any consideration of the evidence of beryllium disease among long-term plant workers must take into account the concentrations prevalent during these earlier years.

**TABLE 7-1 Summary of Beryllium Concentrations at BWI, Elmore, 1958-1962 (Daily Weighted Averages)**

Calendar Year	Number of Samples Within Concentration Interval ( $\mu\text{g}/\text{m}^3$ )					
	<2	2-5	5-10	10-20	20-50	>50
Breathing Zone Samples						
1958	0	6	5	4	2	0
1959	0	3	4	7	4	1
1960	2	8	13	9	10	0
1961	16	3	3	1	1	0
1962	1	4	2	3	2	1
General Area Samples						
1958	34	7	7	5	5	0
1959	3	12	4	3	2	0
1960	10	12	1	0	0	0
1961	16	1	1	0	0	0
1962	7	11	0	0	0	0

Source: NIOSH, 1972.

Analyses were made by BWI of the relationships between the actual and potential DWAs and beryllium production in each operation (Zeuhlike, 1982). In some circumstances, a positive correlation existed between quarterly DWAs, especially potential DWAs, and beryllium production. In many, if not most, operations, however, no statistically significant correlation was observed. Other procedures established at Elmore to minimize worker exposure include issuing a complete set of clean work clothing each day, supplying outer garments, safety shoes, and boots as needed. A respiratory protection program also is in place, with respirators required in specified high-potential exposure areas. Flagrant violation of this requirement can lead to dismissal of an employee.

An outdoor monitoring program is in place to verify compliance with EPA's 0.01  $\mu\text{g}/\text{m}^3$  standard. Nine high-volume monitors are located between 1700 and 18,000 ft from the plant. The last excursions in excess of 0.01  $\mu\text{g}/\text{m}^3$  EPA standard were at different times in June 1984: one from an in-plant equipment failure ( $0.0208 \mu\text{g}/\text{m}^3$  at 3010 ft away) and the other from a low-level stack emission ( $0.0260 \mu\text{g}/\text{m}^3$  at 12,000 ft away); these were with eight to nine monitoring stations operating. No excursions have been recorded since 1984.

#### Rocky Flats, Golden, Colorado

An extensive environmental control and monitoring program has been in place at the Rocky Flats plant since the onset of beryllium use in that facility. The primary beryllium work at Rocky Flats is the machining of unfinished metallic parts into their final shape. Laboratory-scale operations are conducted to develop or analyze specific metallurgical processes. Currently, three work environment monitoring systems are used: personal breathing-zone samples to assure compliance with exposure, fixed-area samples to assure effective operation of control equipment, and swipe samples to assure that adequate housekeeping practices are maintained.

A review of samples taken during 1983 and 1984 indicates that 11 percent of personal samples exceeded  $2 \mu\text{g}/\text{m}^3$ , 31 percent were between 1 and  $2 \mu\text{g}/\text{m}^3$ , and 58 percent were less than  $1 \mu\text{g}/\text{m}^3$ . Virtually all of the values in excess of  $2 \mu\text{g}/\text{m}^3$  were the result of short-term exposures during polishing of nearly finished metal (F. J. Furman, personal communication, April 1988). Recently, the environmental control system has been substantially improved. A low-volume, high-velocity exhaust system was installed, and enclosures were built around potential sources of contamination to minimize worker exposure. Workers are required to wear respirators during any hand-polishing operations; in many cases, such operations have now been eliminated. Recent values of time-weighted average exposures have averaged about  $0.1 \mu\text{g}/\text{m}^3$  during machining operations.

The levels measured during 1983 and 1984 were deemed by the plant

industrial hygienist to be characteristic of concentrations from the late 1970s. Environmental control measures were improved during the 1970s, but higher concentrations might have prevailed during earlier plant operations. Historical data available at the plant are being reviewed, but an analysis is not yet complete.

NIOSH conducted a health hazard evaluation of the Rocky Flats facility during 1984 and 1985 as the result of a diagnosis of beryllium disease in an employee (NIOSH, 1986). Personal lapel samples were collected during January and November of 1985. During the January period, the time-weighted average (TWA) sampling results were reported for 31 machinists and 2 laundry workers. The concentrations for 16 of the collected samples were below the analytical detection limit (about  $0.2 \mu\text{g}/\text{m}^3$  for full shift sampling), and all but one of the remainder ranged from 0.20 to  $0.92 \mu\text{g}/\text{m}^3$ . One worker's 8-hour TWA sample was  $7.2 \mu\text{g}/\text{m}^3$ , presumably from polishing a metal part. Of 35 area samples collected during January, 13 had undetectable amounts of beryllium and the remainder ranged from 0.03 to  $0.50 \mu\text{g}/\text{m}^3$ . Nine 8-hour TWA breathing zone samples collected during November on machinists ranged from 0.4 to  $2.1 \mu\text{g}/\text{m}^3$ .

The results of the NIOSH sampling indicated general compliance with the existing OSHA standard. Excursions nevertheless occurred at an unacceptable frequency. Control improvements were implemented that brought concentrations well within regulatory limits. Nonetheless, the NIOSH sampling indicates the dilemma faced in attempting to associate the observed beryllium disease and immunological abnormalities among Rocky Flats employees with specific beryllium concentrations. If the 3 days of sampling are characteristic of the previous 10 years, then there was general compliance with the  $2 \mu\text{g}/\text{m}^3$  standard. However, a specific individual periodically could have had an exposure substantially beyond that of the OSHA limit. Because daily monitoring of each worker was not conducted, it cannot be ruled out that those affected were occasionally, or perhaps often, exposed to 8-hour TWA concentrations substantially above the current standard. Efforts to characterize the exposure of six workers who had an abnormal lymphocyte transformation test at Rocky Flats have been attempted, but satisfactory results have not been obtained.

#### Royal Ordnance Factory, Cardiff

The environmental control practices at a beryllium production facility at the Royal Ordnance Factory (ROF) have been described (British Defense Staff, 1986). A work force of approximately 100, including 14 engaged primarily in cleaning activities, is employed at the facility. Specific daily, weekly, and monthly cleaning tasks are required; for example, all floors are wet-mopped daily and vacuum-scrubbed every other day, while walls are cleaned monthly to a height of 7 ft. Plant conditions are continuously monitored by health physics personnel. Approximately 3000

swipe samples and 5000 personal and area samples are taken monthly in the monitoring program! This effort is supported by six individuals from the Health Physics Department. Each morning selected area samples are analyzed to determine if conditions for that day are satisfactory. Table 7-2 gives the distribution of beryllium concentrations during 1984 and 1985. As can be seen, low levels are maintained in the machine shops, whereas, in the powder stages and plasma spray operations, approximately 2 percent of the samples exceed 2  $\mu\text{g}/\text{m}^3$ , despite the substantial efforts of the control program.

Standards for surface contamination, as measured by swipe samples, are that it should be less than 25  $\mu\text{g}/\text{ft}^2$  in production areas and even lower in laboratories and nonproduction areas. Results for 1984 and 1985 indicate that 95 percent of the samples in both the old and new machine shops met the established goals, as did approximately 90 percent of the samples in the casting and press shop and 75 percent of those in the plasma spray operation. These efforts are indicative of the type of improvement that can be achieved by more detailed housekeeping procedures and monitoring of the workplace. Continued close liaison by DOE with ROF, Cardiff, is recommended.

TABLE 7-2 Annual Summary of Beryllium Air Samples (Static)

Location	Year	Percent of Samples Within Beryllium Concentration ( $\mu\text{g}/\text{m}^3$ ) Interval			
		<0.2	0.2-1.0	1.0-2.0	>2.0
Old machine shop	1984	98.0	1.79	0.09	0.12
	1985	97.6	2.13	0.22	0.05
New machine shop	1984	99.0	0.89	0.10	0.01
	1985	99.3	0.44	0.03	0.23
Powder stages	1984	74.0	22.0	2.50	1.50
	1985	82.0	15.0	1.80	1.10
Plasma spray	1984	80.5	16.0	1.30	2.20
	1985	81.8	15.17	1.54	1.49

Source: ROF, Cardiff, presentation at Los Alamos, September 16-17, 1986

## BERYLLIUM SAMPLING STRATEGIES

### Sampling Protocols

Considerable controversy exists between BWI on the one hand and OSHA and NIOSH on the other regarding the appropriate sampling method for exposure control and regulatory evaluation in the beryllium industry. The company has routinely used a modification of the AEC sampling protocol, which was developed in the early 1950s. [The AEC protocol appears to provide a DWA for a particular job in a plant operation (NIOSH, 1972), whereas the BWI protocol would appear to give a DWA for all workers at an operation.] The BWI protocol places heavy reliance on the use of general area high-volume samplers located in the work areas of particular plant operations, supplemented by short-term (2- to 5-minute) high-volume breathing-zone samples for short-duration work activities. This provides data on the average exposure to all personnel employed at a particular plant operation. Information on an individual worker's average exposure is obtainable only by using a detailed analysis of his work activities during a typical day and from appropriate sampling results.

Alternatively, NIOSH and OSHA specify a sampling protocol in which individual monitors are attached to the lapels of workers and air is drawn through them by means of a battery-operated vacuum pump. When used for an entire working day, the personal sampling scheme provides information on the exposure of the sampled individual throughout whatever tasks may be undertaken during a working day or on a particular job within a plant operation. For regulatory purposes, sampling priorities would be directed toward those workers expected to experience the highest concentrations.

One of the evident advantages of the BWI method is that it focuses on the effectiveness of controls for each plant operation. This method also has been used for more than 30 years in the industry and at BWI, thereby providing a backlog of data to which current and future air measurements can be related. The disadvantage of the method is that monitoring results for individuals can only be obtained by a separate analysis of their work activities during the day and use of appropriate sampling data. Another disadvantage is the emphasis placed on routine work activities and the individuals performing those tasks. It generally does not obtain information on individual worker exposure during upset conditions; some of these conditions are reflected in the area samples. Thus, data are lacking on the exposures of maintenance personnel, who may be highly exposed episodically during equipment failure at any of several work stations. The use of the BWI method also requires a detailed analysis of the work activities of all individuals involved in a particular operation. Verification of this analysis by regulatory personnel requires extensive, time-consuming observations.

The advantage of the personal lapel-monitoring procedure is its direct relationship to individual exposures. All activities of concern can be directly monitored easily, both by company and regulatory personnel. A disadvantage of the personal monitoring method is the resistance of workers to wearing vacuum pumps. Further, personal sampling results, taken for regulatory purposes, may be inappropriate for exposure estimates in epidemiological studies, as they often reflect only the exposures of workers in jobs of special concern.

#### Sampling Accuracy and Precision

Separate from the general advantages and disadvantages of a particular sampling method, it is important that the results accurately reflect what is intended to be measured. NIOSH sponsored a study by BWI to evaluate the accuracy, precision, and comparability of personal lapel monitors and BWI's currently used high-volume samplers. This evaluation of air-sampling techniques was divided into four studies:

1. Lapel total dust, lapel respirable dust, and "AEC 1-day" (high-volume area and breathing zone) measurements taken simultaneously. This was carried out at 20 operations and repeated an average of approximately 18 times during the 1-year study period, yielding 360 full sets of readings that were subject to comparison.
2. Two lapel total dust samplers, one on each lapel, worn by the worker. The test was carried out once at each of the 20 operations.
3. Similar to Study 2, except that lapel respirable samplers were used.
4. A lapel total-dust, lapel respirable-dust, and high-volume sampler were operated simultaneously on a test stand; 8-hour general air samples were collected once at each of the 20 locations.

The results of Study 1 were published by NIOSH (1976). The analysis focused on the average concentrations measured in five work areas, each consisting of one to eight plant operations. The analysis revealed that there were significant differences between total dust concentrations measured by personal samplers and DWA estimates made from 1-day area and breathing-zone high-volume sampling. Regression analysis compared the logarithms of the concentrations from both the personal respirable samples and personal total samples with the high-volume data. The results suggested that at  $2 \mu\text{g}/\text{m}^3$ , measured by the DWA method, the predicted personal respirable sample value would be  $0.92 \mu\text{g}/\text{m}^3$  and the personal total value would be  $2.99 \mu\text{g}/\text{m}^3$ . However, the 95 percent confidence interval for a single predicted value was from  $0.63$  to  $14.31 \mu\text{g}/\text{m}^3$ , indicating the substantial variability of the data. Furthermore, the regression equations had large intercept values at zero DWA concentration. This could indicate

the presence of a systematic error in one of the sampling methods, or it could be the result of the large uncertainties present in the individual sample values.

Nevertheless, without resolving the origin of the substantial differences between the sampling techniques, the NIOSH report recommended that a personal sampling method be used, "since the AEC method is not a practical method for monitoring a beryllium facility for regulatory purposes."

Following publication of the NIOSH report, BWI contracted with Equitable Environmental Health Inc. to analyze the same data and with New York University to undertake laboratory measurements to identify the possible source of differences between DWA results and that from personal lapel samplers.

#### *Equitable Environmental Health Analysis*

The analysis by Equitable Environmental Health (EEH) confirmed that significant differences existed (EEH, 1977). In its analysis of sampler differences, however, EEH calculated *arithmetic averages* of the ratio between lapel totals and DWA results, rather than *geometric averages*, as being appropriate for an analysis of ratios. This procedure overemphasized the differences between the two sampling methods. It would appear that the NIOSH regression analysis better represented the problem.

The EEH analysis does add further information on the usefulness of the different sampling methods. The analysis of 16 pairs of lapel samples (Study 2) by EEH indicated a high variability in both the total and respirable sampling data. It also indicated that the precision of the measurement at a value of  $1 \mu\text{g}/\text{m}^3$  would be approximately 67 percent rather than the precision specified by OSHA for regulatory purposes of 25 percent at the control limit. The 95 percent confidence level for a 15-minute sample at  $5 \mu\text{g}/\text{m}^3$  was 80 percent.

In conjunction with the EEH analysis, BWI undertook an independent study of the precision of total-dust lapel and high-volume samplers in a test-stand experiment. Nine personal and nine high-volume samplers were located adjacent to one another on a test stand in five workplace locations, and the variability of the measured concentrations was analyzed. Data from one location were considered inappropriate because a fire occurred at the site during sample collection and atypically high concentrations were recorded. Analysis of the remaining lapel samplers indicated that there was an 85 percent probability that the precision was within the desired OSHA limits. A corresponding analysis of the high-volume samplers indicated an even higher precision. The latter analysis, however, was biased in that a second data set was deleted from consideration solely on the basis that its standard deviation was greater than that of other sets.

Further, a substantial source of variability in the high-volume samples may be from fluctuations in line voltage over time (see NYU experiments). No consideration or measurement of this possible effect was made in these studies. It would not have been detected in this sampling experiment. It is obvious that a full understanding of the contributions to inter- and intra-sample variability is not in hand. Additional sampling methodology research is clearly called for.

#### *New York University Experiments*

Several experiments were undertaken by the Institute of Environmental Medicine at New York University (NYU) to investigate the possible origin of the 50 percent difference in total dust sample results obtained by lapel monitors and those calculated from high-volume samplers (Cohen et al., 1984; Bohne and Cohen 1985; Cohen and Positano, 1986). Various sampler effects were investigated (inlet effects, filter efficiency, self-dilution, electrostatic charging) and were found not to contribute measurable bias to personal sampler exposure estimates. However, dust resuspended from that deposited on clothing fabric was found to be a potential contributor to the concentration breathed by workers (Bohne and Cohen, 1985). Higher beryllium concentrations were measured by personal samplers mounted on mechanically shaken contaminated fabrics than by personal samplers a short distance from the fabrics, which was representative of nose breathing. The clothing samples were contaminated by hanging unused material on a wall in a dusty plant area for up to 48 hours. The fabric-mounted sampler results were 28 percent higher for cotton fabric and 41 percent higher for aramid fabric than corresponding sampler results representing nose breathing-zone concentrations. The ranges of the five pairs of samples in each fabric set were, respectively, 10 to 48 percent and 8 to 74 percent.

A separate experiment, conducted in a small glove box, measured the amount of beryllium released from aramid fabric shirts used for a work shirt (Cohen and Positano, 1986). The amounts of beryllium released from material from two washed shirts and from two unwashed relatively new shirts were negligible, even though some of the shirts were contaminated to a level more than 30 times that of the previous experiment. Material from two unwashed old shirts, however, was found to generate air concentrations of 0.20 and 0.64  $\mu\text{g}/\text{m}^3$ . Information was not available on the past uses of the study shirts. The data from the NYU experiments, although limited, demonstrate that there can be a contribution to worker exposure from particles released from worker's clothing. However, its overall contribution to worker exposure is uncertain. It would appear, nevertheless, that the magnitude of the contribution would be inadequate to explain the difference between lapel and hand-held high-volume samplers, except for very low exposure situations.

A notable result of the NYU experiments is that the magnitude of the potential exposure from clothing, as measured by either fabric-mounted or

nearby monitors, is much greater than the difference between the two monitors in any particular experiment. The magnitude of clothing-related exposures in the actual work environment is not known. Its possible contribution needs further investigation, such as by monitoring a worker using unwashed clothing in otherwise unexposed circumstances. If the clothing-related exposure is found to be substantial, it could be reduced by more frequent clothing changes or by use of fabrics that release less beryllium.

Another significant finding of the NYU study was that line voltage fluctuations contributed to a reduction in flow in the high-volume samplers (Cohen et al., 1984). The voltage reductions could yield concentrations that were only 70 percent of those actually present. This is of the magnitude of the difference between the sampling techniques measured in NIOSH experiments. It is not clear whether such line voltage fluctuations affected past routine measurements or whether present measurements might be affected. A systematic study of the Elmore electrical system should be undertaken and continued as necessary. If line fluctuations are common in any sections of the plant, voltage stabilizers should be used during sampling. Alternatively, an appropriately designed sampling train, with a critical orifice, can be used to maintain proper flow. Care should be taken, however, to assure an adequate air flow into the Whatman filter, as any reduction in flow below that nominally used will result in reduced filter efficiency as well as lower collection volume (Cohen et al., 1984).

#### APPLICABLE REGULATIONS

The current OSHA permissible exposure limits (PEL) are  $2 \mu\text{g}/\text{m}^3$  averaged over an 8-hour period,  $5 \mu\text{g}/\text{m}^3$  as a 30-minute ceiling, and  $25 \mu\text{g}/\text{m}^3$  as a peak (no time period for measurement specified). The  $2 \mu\text{g}/\text{m}^3$  value was the standard initially adopted by the AEC in the early 1950s, and it was incorporated in the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit List in 1955, then adopted by OSHA as a consensus standard in 1971. NIOSH has proposed an 8-hour TWA PEL of  $0.5 \mu\text{g}/\text{m}^3$  (NIOSH, 1977). The NIOSH recommendation was based on the agency view that there was substantial evidence of beryllium carcinogenicity in animals, although limited evidence of carcinogenicity in humans. In 1977 OSHA proposed reducing the TWA to  $1.0 \mu\text{g}/\text{m}^3$ , but the proposal was withdrawn. Recently OSHA has proposed reducing the standards for 432 materials for which lower NIOSH or ACGIH recommendations were published (OSHA, 1988). Beryllium was not included in the list because "To consider the carcinogenic effects of beryllium, OSHA would have to perform a quantitative risk assessment, which could not be completed in time for this rulemaking." OSHA later may wish to reconsider the beryllium standard, based on recently published studies of cancer risk (IARC, 1987) and the new immunological findings discussed elsewhere in this report.

The International Agency for Research on Cancer (1987) and the National Toxicology Program (1985) both deem that there is sufficient evidence of carcinogenicity of beryllium and beryllium compounds in animals and limited evidence of carcinogenicity in humans. Such a designation invokes the requirements of OSHA's hazard communication rule, as does the finding of acute and chronic pulmonary disease (OSHA, 1987). The EPA's Carcinogen Assessment Group rates beryllium in all its forms as a probable human carcinogen. Table 7-3 lists the various EPA regulations applicable to beryllium and its compounds. Beyond these regulations, no beryllium-specific regulations would appear to be forthcoming because of environmental concerns for exposures outside the plant grounds.

### CONCLUSIONS AND RECOMMENDATIONS

There are two health conditions of concern that are associated with beryllium metal production--chronic berylliosis and lung cancer. There is reason to believe that neither condition represents a threshold process--i.e., where exposures less than a threshold concentration would be completely safe. There is no basis today for knowing how safe an occupational exposure is with respect to chronic berylliosis at the 2  $\mu\text{g}/\text{m}^3$  level. The estimated lung cancer risk at the 2  $\mu\text{g}/\text{m}^3$  standard is small but not negligible. Given these considerations, it would be appropriate to reduce the occupational exposure to the maximum extent feasible.

The majority of cases of severe beryllium disease have been the result of substantial exposures to the metal and its compounds during the early years of beryllium production and processing. While individual exposures often cannot be substantiated, air concentrations of as much as 100 times those now observed were common during early beryllium operations. In recent years, the finding of immunological changes, often unaccompanied by clinical impairment but with microscopic evidence of granulomatous disease, have occurred in facilities largely in compliance with the 2  $\mu\text{g}/\text{m}^3$  standard. Nevertheless, the possibility exists that affected individuals were exposed episodically to concentrations substantially above the current standard.

Notable achievements have been accomplished in Great Britain and at Rocky Flats in maintaining TWA exposures well below the 2  $\mu\text{g}/\text{m}^3$  standard. These have been the result of installing state-of-the-art engineering controls and extensive area and personal monitoring, including the use of swipe samples, and substantial efforts have been devoted to the maintenance of clean factory facilities. The difficulties of applying such extensive control measures in a large production facility such as BWI's Elmore plant are clear, and some controls may be impractical. Nevertheless, substantial improvements are possible in the control and monitoring of beryllium in the workplace. Process changes and improvements already

**TABLE 7-3 EPA Beryllium Regulations**

Regulatory Action	Effect of Regulation; Other Comments
40 CFR 61.30 et seq.; 61.40 et seq. 4/6/73. CAA, 112: NESHAP promulgated for extraction and production sites for beryllium and beryllium oxide, and beryllium rocket-motor firing.	Under continuing assessment to determine efficacy of existing rule; source assessment completed, 5/80.
45 FR 79318. 11/28/70. CWA, 304(a): Water quality criteria for dissociated beryllium published in final form.	Under review for possible revision.
40 CFR 117.3, 117.13. Promulgated 8/9/79. CWA, 311: Beryllium chloride and beryllium fluoride. Hazardous spill regulation establishing reportable quantity (5000 lb, 2270 kg) and imposing reporting requirements.	Not based on carcinogenicity. Encourages greater care in handling and shipping of chemicals.
40 CFR 261.10. Promulgated 5/19/80. RCRA, 3001-3004: Subjects waste known to contain beryllium and beryllium compounds to handling and report and record-keeping requirements.	
40 CFR 261.33. Promulgated 5/19/80. RCRA, 3001-3004: Subjects beryllium dust as waste products; also subjects off-specification batches and spill residues in excess of 100 kg to handling and report and record-keeping requirements.	Based on toxic effects other than acute. The Carcinogen Assessment Group at EPA has included this chemical on its list of potential carcinogens. As a result of this listing, beryllium dust is regulated under the hazardous waste disposal rule of the Resource Conservation and Recovery Act.
50 FR 13456. Promulgated 4/4/85. CERCLA, 101(14): Final rule designates and establishes reportable quantity of 1 lb for beryllium and 5000 lb for beryllium chloride and beryllium fluoride.	Provides control over releases of these chemicals into the environment. Beryllium chloride and beryllium fluoride are also governed by a CWA 311 hazardous spill regulation with reportable quantities identical to those listed under CERCLA.

have substantially lowered beryllium concentrations. Further reductions can be achieved by additional improvements in existing exhaust ventilation systems and beryllium particulate control procedures.

Based on these findings, the committee recommends the following:

- Implement a substantially expanded and improved monitoring program, including the use of personal samplers. This includes undertaking research to identify sources of variability in monitoring techniques and what measures should be taken to reduce them. Sources of exposure to workers, including release from clothing, should be part of the study.
- Increase the number of housekeeping personnel and undertake improved housekeeping activities, including monitoring work areas with the use of swipe samples.
- Undertake a complete review of the plant exhaust ventilation system, preferably by outside consultants who have particular expertise in low-volume, high-velocity ventilation systems.
- Conduct a continuing review of beryllium processing technology with a view to maintaining beryllium production facilities with state-of-the-art engineering that minimizes human exposure to beryllium and its compounds.
- Implement an expanded medical monitoring program that makes use of lymphocyte transformation on circulating blood and appropriate follow-up of abnormal individuals. This includes the design of plant work force surveillance activities with a view to their use in epidemiological evaluations of beryllium disease dose and time-response relationships. This would require monitoring data that allow information to be developed on plant exposures to individual workers.
- Initiate research to develop improved monitoring techniques, with emphasis given to the development of "real time" monitoring devices.

#### REFERENCES

Bohne, J. E., and B. S. Cohen. 1985. Aerosol resuspension from fabric: Implications for personal monitoring in the beryllium industry. *Am. Ind. Hyg. Assoc. J.* 46:73-79.

British Defense Staff. 1986. Beryllium supply program. Memorandum to R. J. Jiaoletti from J. Reichelt, Washington, D.C. (October 16).

Cohen, B. S., N. H. Harley, and M. Lippmann. 1984. Bias in air sampling

techniques used to measure inhalation exposure. *Am. Ind. Hyg. Assoc. J.* 45:187-192.

Cohen, B. S., and R. Positano. 1986. Resuspension of dust from work clothing as a source of inhalation exposure. *Am. Ind. Hyg. Assoc. J.* 47:225-258.

Equitable Environmental Health Inc. 1977. Analysis of the Comparability and Precision of Lapel and High Volume Samplers in Air Sampling for Beryllium. Berkeley, Calif.

International Agency for Research on Cancer. 1987. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Supplement 7:127-128. Lyon, France.

Kaczynski, D. J. 1986. Research and Development Study for Optimization of Beryllium Production Operations, Task V, Final Report. Contract DE-AC04-82AL18071, Brush Wellman Inc., Elmore, Ohio (July).

Kriebel, D., J. D. Brain, N. L. Sprince, and H. Kazemi. 1988. State of the art: The pulmonary toxicity of beryllium. *Am. Rev. Respir. Dis.* 137:464-473.

Kreiss, K., L. Newman, M. Mroz, and P. Campbell. 1988. Screening blood test identifies subclinical beryllium disease. *Am. Rev. Respir. Dis.* 137(Suppl):97.

National Institute for Occupational Safety and Health. 1972. Criteria for a Recommended Standard...Occupational Exposure to Beryllium. HSM 72-10268.

National Institute for Occupational Safety and Health. 1976. Beryllium Sampling Methods: Comparison of Two Personal Sample Collection Methods With the AEC Sample Collection Method as Used for One Year in a Beryllium Production Facility (by H. M. Donaldson and W. T. Stringer). HEW Publication No. (NIOSH) 76-201, Cincinnati, Ohio (July).

National Institute for Occupational Safety and Health. 1977. Statement of Edward J. Baier, Deputy Director of NIOSH-CDC, at Public Hearing on the Occupational Standard for Beryllium (August).

National Institute for Occupational Safety and Health. 1986. Health Hazard Evaluation Report: Rockwell International, Golden, Colorado. HETA 84-510-1691 (May).

National Toxicology Program. 1985. Beryllium and certain beryllium

compounds. Pp. 93-96 in Fourth Annual Report on Carcinogens. NTP 85-001:93-96, Research Triangle Park, North Carolina.

Newman, L., K. Kreiss, T. E. King, S. Seay, and P. Campbell. 1989. Pathologic and immunologic alterations in beryllium disease: Re-examination of disease definition and natural history. Am. Rev. Respir. Dis., in press.

Occupational Safety and Health Administration. 1987. Hazard Communication: Final Rule. Federal Register 52:31852-31886 (August 24).

Occupational Safety and Health Administration. 1988. Air Contaminants: Proposed Rule. Federal Register 53:21194 (June 7).

Roszman, M. D., J. A. Kern, J. A. Elias, M. R. Cullen, P. E. Epstein, O. P. Preuss, T. N. Markham, and R. P. Daniele. 1988. Proliferative response of bronchoalveolar lymphocytes to beryllium: A test for chronic beryllium disease. Ann. Internal. Med. 108:687-693.

Sterner, J. H., and M. Eisenbud. 1951. Epidemiology of beryllium intoxication. Arch. Ind. Hyg. Occup. Med. 4:123-151.

U. S. Environmental Protection Agency. 1987. Health Assessment Document for Beryllium. EPA/600/8-24/026F, Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Research Triangle Park, North Carolina.

Zuehlke, J. R. 1982. Research and Development Study for Optimization of Beryllium Production Operations: Task I, Review of Current Operations. Contract DE-AC04-82AL18071, Brush Wellman Inc., Elmore, Ohio (July).

## **Appendix A-1**

EXCERPTS FROM  
P-110-R2, June 25, 1981  
(Supersedes P-110-R1, January 30, 1971)  
NATIONAL STOCKPILE  
PURCHASE SPECIFICATION

Published by  
U.S. Department of Commerce

With Approval of  
Federal Emergency Management Agency

### **BERYLLIUM METAL, VACUUM CAST INGOT**

#### **DESCRIPTION**

This specification covers vacuum cast beryllium metal produced by means of the magnesium reduction of beryllium fluoride or the electrolytic reduction of beryllium chloride and the subsequent vacuum casting of the resulting beryllium metal into ingots.

#### **CHEMICAL, IMPURITY COEFFICIENT, AND PHYSICAL REQUIREMENTS**

All beryllium metal purchased under this specification shall be in lots of ten ingots and shall conform to the following chemical, impurity concentration, and physical requirements.

##### **Chemical and Impurity Coefficient Requirements:**

1. Each ingot shall conform to the following chemical and impurity coefficient requirements:

	<u>Grade A</u>	
	<u>Percent</u> <u>(By Weight)</u>	<u>Impurity</u> <u>Coefficient</u>
Beryllium (By Difference)      (Be)	Min.      99.0	-

Beryllium Oxide plus Beryllium Nitride	(BeO+Be <sub>3</sub> N <sub>2</sub> )	Max.	1.0	-
Aluminum	(Al)	Max.	0.14	7.7
Iron	(Fe)	Max.	0.13	41.
Carbon Total	(C)	Max.	0.12	-
Magnesium	(Mg)	Max.	0.12	2.2
Titanium	(Ti)	Max.	0.05	-
Nickel	(Ni)	Max.	0.04	71.
Chromium	(Cr)	Max.	0.03	49.
Manganese	(Mn)	Max.	0.02	217.
Sodium	(Na)	Max.	0.02	-
Lithium	(Li)	Max.	0.0003	9,200.
Cadmium	(Cd)	Max.	0.0002	24,000.
Boron	(B)	Max.	0.0002	62,900.

<sup>1</sup>The total impurity concentration (TIC) is the sum of the products of the percent by weight of each element and its corresponding impurity coefficient. The TIC for the elements listed above with an impurity coefficient shall not exceed 24.0.

2. A composite sample of ten ingots whose content is proportionate to the weight of each ingot shall conform to the following chemical requirements:

		<u>Grade A</u>
		Percent
		(By Weight)
Beryllium Oxide	(BeO)	Max. 0.5 <sup>1</sup>
Iron	(Fe)	Max. 0.11 <sup>1</sup>
Carbon	(C)	Max. 0.10 <sup>1</sup>
Aluminum	(Al)	Max. 0.08 <sup>1</sup>
Magnesium	(Mg)	Max. 0.10 <sup>1</sup>
Silicon	(Si)	Max. 0.06
Nitrogen	(N)	Max. 0.04
Calcium	(Ca)	Max. 0.02
Zinc	(Zn)	Max. 0.02
Copper	(Cu)	Max. 0.015
Chlorine	(Cl)	Max. 0.005
Fluorine	(F)	Max. 0.005
Lead	(Pb)	Max. 0.002
Molybdenum	(Mo)	Max. 0.002
Silver	(Ag)	Max. 0.001
Cobalt	(Co)	Max. 0.001

<sup>1</sup>The percentages for these elements may be computed as a weighted average of the results of the tests in [the ingot analysis section].

Any metallic impurity not listed above shall not exceed 0.04 percent by weight.

The total of the following impurities in the composite sample shall not exceed 0.15 percent by weight: cobalt, nickel, copper, germanium,

strontium, zirconium, molybdenum, silver, tin, barium, hafnium, tantalum, tungsten, gold, thallium, lead, thorium, uranium, gallium, and columbium.

The seller shall meet the (a) minimum value for beryllium by difference and (b) maximum impurity limits for all other items listed in [the ingot analysis and composite analysis sections] of this specification.

Physical Requirements

All beryllium metal shall be in the form of cylindrical vacuum cast ingots nominally twelve to fifteen inches length, weighing approximately 400 pounds. The top surface shall not extend beyond the cylindrical surface of the ingot (cauliflower head). Ingots shall be cropped to remove the slag top. The top surface of the ingot shall be parallel with the bottom surface (maximum allowable slope one inch from the horizontal). All surfaces of each ingot shall be cleaned by mechanical or chemical methods to leave the surface of the ingot free of slag, carbides, etc. Before adopting a technique, it must be shown by the seller that the treatment used does not alter the chemical composition of the surface so that a sample taken from the treated surface will fail to meet the chemical requirements set forth in [the ingot analysis section]. In the case of chemical treatment particular care must be taken to avoid the entrapment of reagents in cracks, fissures, etc., in the ingot.

**Appendix A-2**

EXCERPTS FROM  
P-110a-R1, May 9, 1984  
(Supersedes P-110A-R, March 25, 1983)  
NATIONAL DEFENSE STOCKPILE  
PURCHASE SPECIFICATION

Published by  
U.S. Department of Commerce

With Approval of  
Federal Emergency Management Agency

**BERYLLIUM METAL, HOT-PRESSED POWDER BILLET**

Grade A  
Type 1 and Type 2

**DESCRIPTION**

This specification covers beryllium metal hot-pressed powder billet suitable for use by the Department of Defense and the Department of Energy in weapon production.

**REQUIREMENTS**

All metal purchased under this specification shall be weldable beryllium in billet form produced by vacuum hot-pressed powder metallurgy.

Recycling of machine chips or scrap beryllium without first remelting shall not be accepted.

Every billet shall be inspected. Any billet which fails to comply with any specification requirement shall be rejected.

The billet shall be 30-36 inches in diameter and 38-46 inches in length.

**Chemical Composition**

Chemical analysis methods to be used must be approved by the procuring activity.

The billet shall comply with the following chemical requirements:

	<u>Percent by Weight</u> (Dry Basis)
Beryllium	Minimum
Beryllium Oxide	Maximum
*Aluminum	Maximum
*Iron	Maximum
Carbon	Maximum
Magnesium	Maximum
Silicon	Maximum
Sulfur	Maximum
Uranium	Maximum
Nickel	Maximum
Chromium	Maximum
Manganese	Maximum
Copper	Maximum
Titanium	Maximum

\*The iron to aluminum ratio shall be maintained within the acceptable window shown in Figure 1.

#### Bulk Density

The billet shall have a minimum bulk density of 99.3% of theoretical density calculated as follows:

$$\text{Theoretical Density} = \frac{100}{\frac{100 - \frac{1}{2} \text{BeO}}{1.847} + \frac{\frac{1}{2} \text{BeO}}{3.009}} \text{ gm/cc}$$

The bulk density test shall be performed on the complete billet prior to Figure 1 to test sample removal.

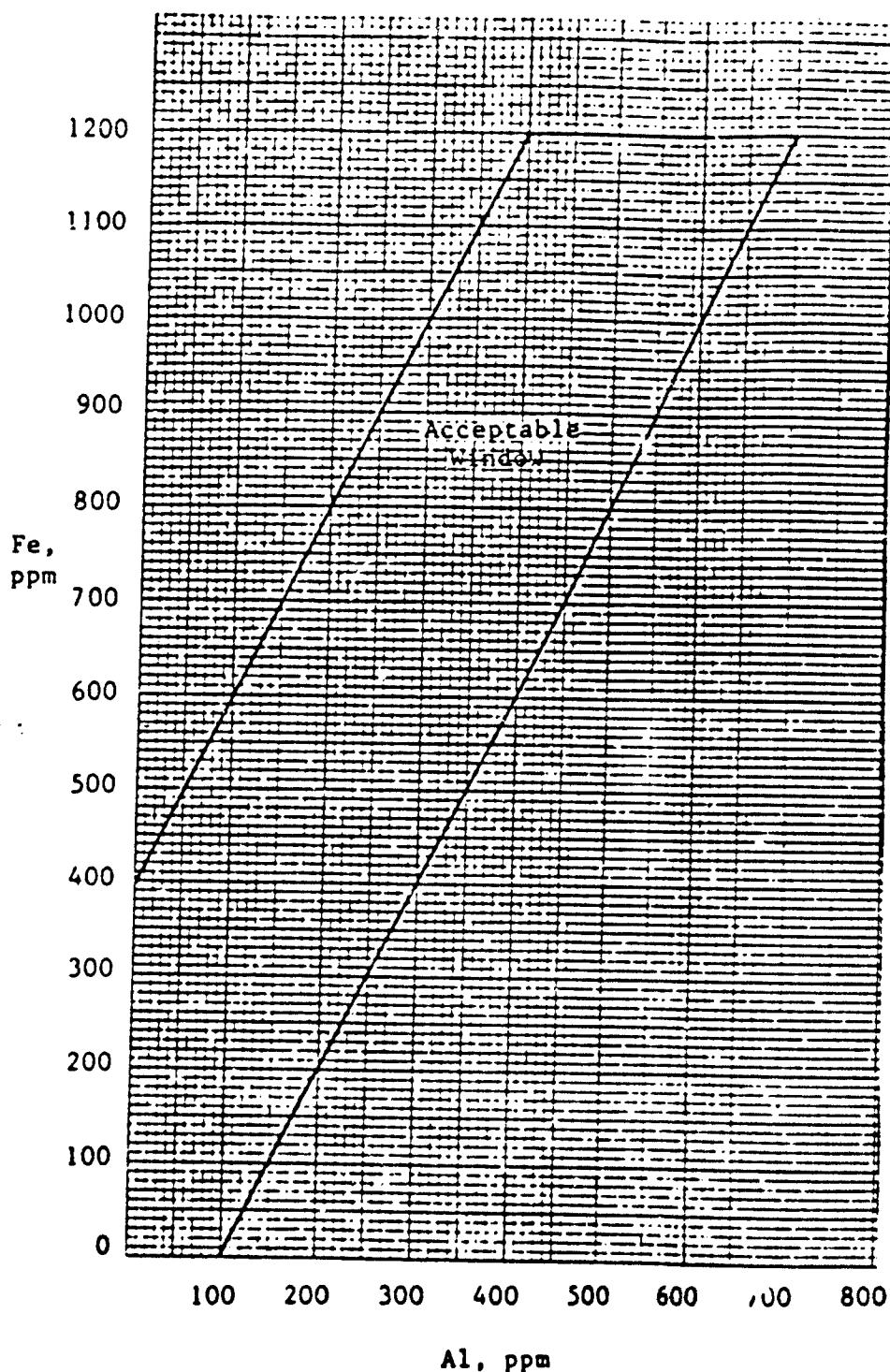


Figure 1

The billet shall be tested by immersion in distilled water at a temperature of 16C to 24C. Measure the actual temperature of the water to within  $\pm 0.6C$  and determine the true density from the following table:

Degrees C	Density (g/cc)	Degrees C	Density (g/cc)
15	0.99913	21	0.99802
16	0.99897	22	0.99780
17	0.99880	23	0.99756
18	0.99862	24	0.99732
19	0.99843	25	0.99707
20	0.99823	26	0.99681

#### Mechanical Properties

The billet shall comply with the following mechanical requirements:

<u>Property</u>	<u>Minimum</u>	<u>Maximum</u>	<u>Direction<sup>1</sup></u>
-----------------	----------------	----------------	------------------------------

#### Room Temperature

\*Yield strength, KSI<sup>2</sup>

Type 1	30	38	L&T
Type 2	28	38	L&T

Ultimate tensile

strength, KSI<sup>2</sup>

40

L&T

Elongation,

percent @ 4 x diameter	1.0	L
	2.0	T

\*Ratio of Yield Strength to  
Ultimate Tensile Strength

0.9

#### 1200F

Elongation,

percent @ 4 x diameter	8.0	T
------------------------	-----	---

-----  
\*Yield strength is tensile strength at the upper yield point or at the 0.2 percent offset, whichever is greater.

<sup>1</sup> L - longitudinal: Long dimension of billet.

T - transverse: Short dimension of billet (diameter).

<sup>2</sup> KSI - thousand psi

Tensile test procedures shall follow MAB-205-M, except tests at room temperature shall be conducted using a constant head motion of 0.0028 inch/minute  $\pm 10$  percent. An extensometer shall be used to measure

strain. The extensometer is not required for tests at 1200F and a faster head motion may be used.

Tensile specimens shall be prepared following MAB-205-M, Section 2. End-loading during machining shall not exceed 5000 psi.

#### Grain Size

The average grain size shall be 25 microns or less using the ASTM intercept technique. The maximum grain size shall be 125 microns.

The metal shall have a uniform grain structure. Duplex grain structure that would reduce the ability of the metal to yield and redistribute stresses shall not be accepted.

Test specimens shall be prepared using ASTM E3. Photomicrographs (4 x 5 inches minimum) taken at 300x magnification shall be prepared using ASTM E2. The average grain size shall be determined using the ASTM E112 intercept technique. The maximum grain size shall be determined from the photomicrograph.

#### Internal and External Condition

The skin of each billet shall be removed to a depth that will expose material complying with specification requirements.

The billet shall be examined for surface defects by fluorescent penetrant inspection using MIL-I- 6866, current revision. The billet shall be free of all cracks and pores greater than 0.010 inch. Three 0.010 inch pores will be permitted within any one-inch circle. Up to 10 pores larger than 0.010 inch in size may be removed by blending to a maximum depth of 0.050 inch.

The billet shall be clean, solid, uniform in quality and condition, free of foreign materials and internal and external imperfections detrimental to the performance of fabricated parts. Ultrasonic discontinuity indications in excess of the response from a 5/64 inch flat-bottomed hole at the estimated discontinuity depth shall not be accepted. Minor surface defects caused by handling will not be cause for rejection.

#### Powder Purity

A random half-pound sample of the final blended powder shall be obtained from each lot prior to pressing. The powder shall be examined by radiographic inspection. The maximum inclusion count shall not exceed the following:

<u>Inclusion Size (Inches)</u>	<u>Frequency (Maximum Permitted)</u>
Greater than 0.005 and up to and including 0.010	100
Greater than 0.010 and up to and including 0.020	8
Greater than 0.020 and up to and including 0.030	4
Greater than 0.030	0

SAMPLING, INSPECTING, AND TESTING

Test specimens for grain size, chemical and mechanical properties shall be taken from samples which have been machined from the top and bottom of the billet. The top sample shall be machined from a core approximately 2-3/4 inches by 3-1/2 inches long which has been removed from the billet center. The bottom sample shall be machined from a chord approximately 1-3/4 inches into the billet.

The number of test specimens to be prepared from the top and bottom sample of each billet shall be the following:

Chemistry:	1 each
Mechanical:	2 each Longitudinal - room temperature
	2 each Transverse - room temperature
	1 each Transverse - 1200F
Grain Size:	1 each

If one or more specimens fail to comply with specification requirements, two additional samples may be tested. If either specimens fails in retest, the billet shall be rejected.

Inspecting and testing shall be under the direction of the procuring activity.

**Appendix A-3**

EXCERPTS FROM  
P-110B, October 18, 1985

NATIONAL STOCKPILE  
PURCHASE SPECIFICATION

Published by  
U.S. Department of Commerce

With Approval of  
Federal Emergency Management Agency

**BERYLLIUM METAL, HOT-PRESSED POWDER BILLET**

Instrument Grades

**DESCRIPTION**

This specification covers beryllium metal hot-pressed powder billet suitable for use by the Department of Defense and other government agencies primarily in guidance components.

**REQUIREMENTS**

All metal purchased under this specification shall be instrument grade beryllium in billet form produced by vacuum hot-pressing beryllium powder<sup>1</sup>.

Every billet shall be inspected. Any billet which fails to comply with any specification requirement shall be rejected.

---

<sup>1</sup>All beryllium acquired under this specification shall conform to the chemical and physical properties identified in this specification. The material may be produced by methods other than vacuum hot-pressing provided written certification of satisfactory performance of the material is provided to the acquiring agency. Written certification of actual satisfactory performance in the intended components shall be obtained from the manufacturer of those components. The written certification shall be obtained by the supplier of beryllium and provided to the acquiring agency prior to contract award.

Chemical Composition

The billet shall comply with the following chemical requirements:

<u>Percent by Weight</u> (Dry Basis)			
		Grade B	Grade C
Beryllium	Minimum	98.0	94.0
Beryllium Oxide		2.2 Max.	5.0 Max.
			4.25 Min.
Aluminum	Maximum	0.10	0.16
Iron	Maximum	0.15	0.25
Carbon	Maximum	0.15	0.25
Magnesium	Maximum	0.08	0.08
Silicon	Maximum	0.08	0.08
Sulfur	Maximum	0.04	0.10
Uranium	Maximum	0.04	0.10
Nickel	Maximum	0.04	0.10
Chromium	Maximum	0.04	0.10
Manganese	Maximum	0.04	0.10
Copper	Maximum	0.04	0.10
Titanium	Maximum	0.04	0.10

Chemical analysis methods to be used must be approved by the acquiring activity.

Bulk Density

The billet shall have a minimum bulk density of 99.6 % for Grade B and 99.3% for Grade C of theoretical density calculated as follows:

$$\text{Theoretical Density} = \frac{100}{100 - \frac{\text{BeO}}{1.847}} \text{ gm/cc}$$

$$= \frac{100}{100 - \frac{1 \text{ BeO}}{3.009}} \text{ gm/cc}$$

The billet shall be tested by immersion in distilled water at a temperature of 16°C to 24°C. Measure the actual temperature of the water within  $\pm 0.6^\circ\text{C}$  and determine the true density from the following table:

Degrees C	Density (g/cc)	Degrees C	Density (g/cc)
15	0.99913	21	0.99802
16	0.99897	22	0.99780
17	0.99880	23	0.99756
18	0.99862	24	0.99732
19	0.99843	25	0.99707
20	0.99823	26	0.99681

### Mechanical Properties

The billet shall comply with the following mechanical requirements:

<u>Property</u>	<u>Strength</u> (KSI Minimum)		<u>Direction</u> <sup>1</sup>
	<u>Grade B</u>	<u>Grade C</u>	
Micro Yield Strength	5	9	L & T
Yield Strength (0.2 percent offset)	40	N/S <sup>2</sup>	L & T
Tensile Strength	55	50	L & T
Elongation, percent in one inch	2.0 min.	N/S <sup>2</sup>	L & T

<sup>1</sup>L - Longitudinal: longitudinal direction is parallel to the direction of pressing.

T - Transverse: transverse direction is perpendicular to the direction of pressing.

<sup>2</sup>Not specified.

### Test Procedures

#### Tensile Test

Tensile test procedures for Grade B shall follow MAB-205-M and ASTM E-8 using an average specimen strain rate of  $0.005 \pm .002$ /inches/inch/minute. An extensometer shall be used to measure strain. Tensile specimens shall be prepared following MAB-205-M, Section 2, and ASTM E-8. End loading during machining shall not exceed 5,000 psi. Micro-yield strength (MYS) for Grades B and C shall be measured using procedures specified by the acquiring activity. MYS test specimens shall conform to and be prepared following MAB-205-M, Section 2 using minimum end loading which, in any case, shall not exceed 3,000 psi. The MYS test specimen shall also be used to determine tensile strength for Grade C. (MAB-205-M, 1966, Evaluation Test Methods for Beryllium, National Academy of Sciences, Washington, D.C.)

#### Grain Size

Maximum grain size shall not be greater than 80 microns. The average size for Grade B shall be 15 microns or less and for Grade C shall be 8 microns or less using the ASTM E-112, Linear Intercept Method.

The metal shall have a uniform grain structure. Duplex grain structure that would reduce the ability of the metal to yield and redistribute stresses shall not be accepted.

#### Billet Size

<u>Grade</u>	<u>Diameter</u>	<u>Length</u>
B	23 to 29 inches	30 to 45 inches
C	15.5 to 18.5 inches	19 to 26 inches

#### Internal and External Condition

The skin of each billet shall be removed to a depth that will expose material complying with specification requirements. The billet shall be examined for surface defects by fluorescent penetrant inspection in accordance with MIL-I-6866, current revision, and shall be free of all cracks and pores greater than 0.010 inch. A maximum of three 0.010 inch pores are permitted in any one inch circle.

A maximum of 10 pores greater than 0.010 inch in size may be removed by blending to a maximum depth of 0.050 inch.

The billet shall be uniform in quality and condition; clean, sound, and free of foreign materials and from internal and external imperfections detrimental to the performance of fabricated parts. Ultrasonic discontinuity indications in excess of the response from 3/64 inch diameter flat-bottomed hole at the estimated discontinuity depth shall not be accepted. Minor surface defects caused by handling shall not be cause for rejection.

#### Powder Purity

A random half-pound sample of the final blended powder shall be obtained from each lot prior to pressing for both grades B and C. The powder shall be examined by radiographic inspection. The maximum inclusion count shall not exceed the following:

<u>Inclusion Size (Inches)</u>	<u>Frequency (Maximum Permitted)</u>
Greater than 0.005 and up to and including 0.010	100
Greater than 0.010 and up to and including 0.020	8
Greater than 0.020 and up to and including 0.030	4
Greater than 0.030	

An inclusion is an X-ray indication whose density is equal to or greater than the film density produced by a 0.030 inch sphere of aluminum examined under the same conditions.

SAMPLING, INSPECTING, AND TESTING

Test samples for chemistry, mechanical properties and grain size should be obtained from edge slices or chords removed from the top and bottom of each pressing. The approximate size is 2.75 inches high by 3.0 inches deep. These chords should be taken at the same circumferential location.

The number of test specimens to be prepared from the top and bottom sample of each billet shall be the following:

Chemistry:	1 each
Mechanical:	2 each Longitudinal
	2 Transverse
Grain Size:	1 each

If one or more specimen fails to comply with specification requirements, two additional samples may be tested. If either specimen fails in retest, the billet shall be rejected.

Inspecting and testing shall be under the direction of the acquiring activity.

## Appendix B

### BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

WILLIAM D. MANLY received a B.S. degree in 1947 and his M.S. in 1949 in metallurgy from the University of Notre Dame. He was associate director of the Oak Ridge National Laboratory metallurgy division from 1949 to 1960 and manager of the gas-cooled motor program there from 1960 to 1964. In 1964 he joined Union Carbide as director of materials technology, later becoming vice president and general manager of its Stellite Division. In the 1970 acquisition of Stellite by Cabot Corporation, he joined Cabot and later became senior vice president and manager of its engineered materials group. He retired from Cabot in 1986 as executive vice president. He is a member of the National Academy of Engineering, a fellow and honorary member of the ASM International (its president in 1973), fellow of the American Institute of Mining, Metallurgical and Petroleum Engineers, and fellow of the American Nuclear Society. He has served on and chaired numerous committees and boards of the National Research Council. His areas of expertise include physical metallurgy, process metallurgy, and technical administration.

ROY E. ALBERT received his A.B. degree in 1943 from Columbia University in biology and his M.D. in 1946 from the City University of New York and then trained in internal medicine. From 1949 to 1951 he was a fellow of the U.S. Public Health Service. He was associated with the Atomic Energy Commission from 1952 to 1954 in both research and administrative capacities; he was chief medical officer in the AEC's Division of Biology and Medicine from 1954 to 1956. He was appointed associate professor at the New York University Medical Center in 1959 and subsequently became professor of environmental medicine and deputy director of the Institute of Environmental Medicine. In 1985 he moved to the University of Cincinnati to his current position as professor and chairman of the Department of Environmental Health. He is a member of the Radiation Research Society, Society of Epidemiological Research, and American Cancer Society. His areas of expertise include radiation and chemical carcinogenesis, aerosol deposition and clearance, and cancer and environmental toxicology.

JAMES E. COYNE received a B.S. degree in 1953 from the University of Notre Dame and his M.S. in 1957 from Rensselaer Polytechnic Institute, both in metallurgy. He worked as a metallurgist at Pratt & Whitney Aircraft of the United Aircraft Corporation from 1953 to 1960. He has been with the Wyman-Gordon Company since 1960, where he held various positions in metals

processing and control before his present position of vice president of quality and engineering. He has served on a number of National Materials Advisory Board committees. He is a member of ASM International, the American Institute of Mining, Metallurgical and Petroleum Engineers, and Forging Industry Educational and Research Foundation and is a registered professional engineer in Massachusetts. His areas of expertise include titanium and nickel-base alloys, microstructural control, effects of plastic deformation on mechanical properties, powder metallurgy, and research administration.

EDWARD J. DULIS received a B.S. degree in 1942 from the University of Alabama in metallurgical engineering and his M.S. in 1950 in materials science from Stevens Institute of Technology. He has also done graduate work at New York University, along with management programs of the American Management Association and Columbia University. He worked as research metallurgist at the Naval Air Station in Philadelphia from 1942 to 1945 and as supervisor at U.S. Steel Corporation from 1945 to 1955. He joined Crucible Inc. of Colt Industries in 1955, was made president of the Crucible Research Center in 1971, and retained that position when it became a division of Crucible Materials Corporation. He was elected to its board of directors in 1988. He is a member of the National Materials Advisory Board and has served on numerous NMAB committees. He is a fellow and former member of the board of trustees of ASM International and a member of the American Institute of Mining, Metallurgical and Petroleum Engineers and the American Powder Metal Institute. His areas of expertise include physical metallurgy, superalloys and titanium alloys development, and high-performance powder metallurgy processes and products.

STANLEY H. GELLES received his B.S. degree in 1952, M.S. in 1954, and Sc.D. in 1957 from the Massachusetts Institute of Technology, all in physical metallurgy. He worked as project leader at Nuclear Metals, Inc., from 1957 to 1963. At the Kennecott Copper Corporation Ledgemont Laboratory he worked as project manager and physical research metallurgist from 1963 to 1968. He was associate chief of the applied metallurgy section at the Battelle Memorial Institute from 1968 to 1975. He formed S. H. Gelles Associates, now Gelles Laboratories Inc., in 1976 and serves as its president. He has served on a number of committees of the National Materials Advisory Board. He is a member of ASM International, the American Institute of Mining, Metallurgical and Petroleum Engineers, American Welding Society, National Asbestos Council, and American Society for Testing and Materials. His areas of expertise include the metallurgy of beryllium, phase equilibria, high-pressure technology, microstructure and properties relationships, and effect of gravity on microstructural development in alloys.

KENNETH B. HIGBIE received a B.S. in 1948 in chemical engineering from Oregon State University. He worked as a chemical engineer at the Bureau of Mines at Albany, Oregon, and Washington, D.C., from 1948 to 1957. He

served as associate director of research for the Beryllium Corporation of America from 1957 to 1961. He rejoined the Bureau of Mines in 1961 as the aluminum and bauxite commodity specialist. In 1973 he became chief of the Division of Solid Wastes and subsequently became deputy director of Research Center Operations in 1975. He retired in 1981 and now consults on metallurgical and environmental topics. He is a member of the American Institute of Mining, Metallurgical and Petroleum Engineers, American Association for the Advancement of Science, Sigma Xi, and American Chemical Society.

LOREN A. JACOBSON received his A.B. degree in engineering science from Dartmouth College in 1960, his M.S. in ceramic engineering in 1962, and a Ph.D. in metallurgy in 1968 from the University of California, Berkley. From 1962 to 1982 he served on active duty with the U.S. Air Force in a variety of materials science and engineering assignments, completing his service as program manager in the Materials Science Division, Defense Advanced Research Projects Agency. From 1982 to 1986 he was a staff member at Lawrence Livermore National Laboratory in the Chemistry and Materials Science Department. Since 1986 he has been a staff member at Los Alamos Laboratory's Materials Science and Technology Division, where he is a project leader for advanced materials and processes. His current research activities involve the application of rapid solidification processing to the development of new beryllium alloys.

NOEL JARRETT received a B.S. degree in 1949 from the University of Pittsburgh and his M.S. in 1951 from the University of Michigan, both in chemical engineering. He joined the Aluminum Company of America in 1951, moving from research engineer in smelting to technical director for chemical engineering research and development, until his retirement in 1986. He is a member of the National Academy of Engineering, American Institute of Chemical Engineers, American Institute of Mining, Metallurgical and Petroleum Engineers, Electrochemical Society, and American Society for Metals. He has served on numerous committees and boards of the National Research Council. His areas of expertise include electrochemical cell development, optimization of the Hall-Heroult process, high-temperature fluid bed reactors, pollution control, and high-purity aluminum via crystallization.

GILBERT J. LONDON received his B.S. degree in 1953 from Drexel Institute of Technology and M.S. in 1955 and Ph.D. in 1959 from the University of Pennsylvania, all in metallurgical engineering. He worked as a metallurgist at the General Electric Company from 1956 to 1959, senior research metallurgist at the Franklin Institute from 1959 to 1970, and manager of metallurgical R&D at Kawecki Berylco Industries from 1970 to 1975. He joined the Naval Air Development Center as branch head of structural materials in 1975. He has served on a number of National Materials Advisory Board committees. He is a member of ASM International, the American Institute of Mining, Metallurgical and Petroleum Engineers, American

Institute for Aeronautics and Astronautics, and Sigma Xi. His areas of expertise include beryllium technology, beryllium alloys, flow and fracture of iron, dispersed hard-particle strengthening of metals, high-purity alloys, and microstrain properties.

WILLIAM J. NICHOLSON received a E.S. degree in 1952 from the Massachusetts Institute of Technology and a Ph.D. in 1960 from the University of Washington, both in physics. He served as instructor at the University of Washington in 1960 and as physicist at the IBM Watson Research Laboratories from 1960 to 1968. In 1964 he was adjunct associate professor at Fordham University. He joined the faculty of Mount Sinai School of Medicine in 1969, becoming Professor of Community Medicine in 1986. He is a Fellow of the New York Academy of Sciences and a member of the Collegium Ramazzini. His areas of expertise include occupational and environmental health, cancer risk assessment, and effects of airborne microparticulates.

MARTIN B. SHERWIN received his B.Ch.E. degree in 1960 from the City College of New York, M.S. in 1963 from the Polytechnic Institute of Brooklyn, and Ph.D. in 1967 from the City University of New York, all in chemical engineering. He worked as a process engineer for the Scientific Design Company from 1960 to 1962, process development engineer at Halcon International Inc. from 1962 to 1964, and lecturer in chemical engineering at the City College of New York from 1964 to 1966. He joined Chem Systems Inc. in 1966 and moved up to vice president of R&D, then managing director of Chem Systems International Ltd. In 1980 he joined W. R. Grace & Co. as director of engineering research and is currently executive vice president of the research division. He is a member of the American Institute of Chemical Engineers and the American Chemical Society. His areas of expertise include the development of new and improved processes for chemicals and chemical products, unit process evaluation, and R&D management.

MORGAN C. SZE received a B.S. degree in 1939 and Sc.D. in 1941, both in chemical engineering from the Massachusetts Institute of Technology. He worked for Universal Trading Corporation, E. I. duPont de Nemours & Co., Hydrocarbon Research Inc., and Foster Wheeler Corporation before joining the Lummus Company in 1961. He served as vice president for technical development at Wheelabrator-Frye Inc. and then at The Signal Companies, Inc., as vice president for process, energy, and environmental technology after Wheelabrator-Frye was merged into The Signal Companies, Inc. He retired at the end of 1985. He is a member of the National Academy of Engineering, American Association for the Advancement of Science, American Institute of Chemical Engineers, American Chemical Society, New York Academy of Science, and Sigma Xi. His areas of expertise include nitrogen fixation, petroleum refining and processing, cryogenics, plant design, and process development.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE								
1a REPORT SECURITY CLASSIFICATION N/A	1b RESTRICTIVE MARKINGS None							
2a SECURITY CLASSIFICATION AUTHORITY N/A	3 DISTRIBUTION/AVAILABILITY OF REPORT Unclassified/Unlimited							
2b DECLASSIFICATION/DOWNGRADING SCHEDULE N/A								
4 PERFORMING ORGANIZATION REPORT NUMBER(S)  NMAB-452	5 MONITORING ORGANIZATION REPORT NUMBER(S)							
6a NAME OF PERFORMING ORGANIZATION National Materials Advisory Board	6b OFFICE SYMBOL (If applicable) NMAB	7a NAME OF MONITORING ORGANIZATION OASD (A&T) PS/OTA						
6c ADDRESS (City, State, and ZIP Code) 2101 Constitution Avenue, N.W. Washington, D.C. 20418	7b ADDRESS (City, State, and ZIP Code) 5203 Leesburg Pike Falls Church, VA 22041-3466							
8a NAME OF FUNDING/SPONSORING ORGANIZATION Dept. of Defense/Dept. of Energy	8b OFFICE SYMBOL (If applicable) DOD/DOE	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER MDA903-87-C-0635						
8c ADDRESS (City, State, and ZIP Code) Washington, D.C.	10 SOURCE OF FUNDING NUMBERS <table border="1"> <tr> <th>PROGRAM ELEMENT NO</th> <th>PROJECT NO</th> <th>TASK NO</th> <th>WORK UNIT ACCESSION NO</th> </tr> </table>				PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO					
11 TITLE (Include Security Classification)  Beryllium Metal Supply Options	→ NMAB, Low weight, High Strength							
12 PERSONAL AUTHOR(S) Committee on Technologies for Preparing Beryllium Metal								
13a TYPE OF REPORT Final	13b TIME COVERED FROM 8/20/87 TO 4/10/89	14 DATE OF REPORT (Year, Month, Day) April 5, 1989	15 PAGE COUNT 124					
16 SUPPLEMENTARY NOTATION								
17 COSATI CODES <table border="1"> <tr> <th>FIELD</th> <th>GROUP</th> <th>SUB GROUP</th> </tr> </table>		FIELD	GROUP	SUB GROUP	18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) 1. Beryllium; 2. Production Facilities; 3. Metallurgical Extraction Techniques; 4. Metallurgical Unit Processing; 5. Scrap Recycling; 6. Health Considerations & Monitoring			
FIELD	GROUP	SUB GROUP						
19 ABSTRACT (Continue on reverse if necessary and identify by block number) The importance of an uninterrupted supply of beryllium metal for the U.S. military and aerospace effort is described and the means by which the single supplier in the western world could meet present and future environmental requirements is examined. Cooperation between government and related activities is suggested. Major recommendations are directed toward upgrading existing facilities and processes for extracting beryllium; use of the gas atomization process in lieu of the current beryllium powder-production method; utilization of near-net-shape technology in making beryllium hardware; establishment of a separate facility for electrorefining, scrap recycling, gas atomization and near-net-shape consolidation; control of DOD scrap; improving the beryllium monitoring system; and the continuation of efforts to reduce worker exposure to beryllium particulates.								
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION Unclassified						
22a NAME OF RESPONSIBLE INDIVIDUAL John E. DuBreuil		22b TELEPHONE (Include Area Code) (703) 756-2310	22c OFFICE SYMBOL OASD					